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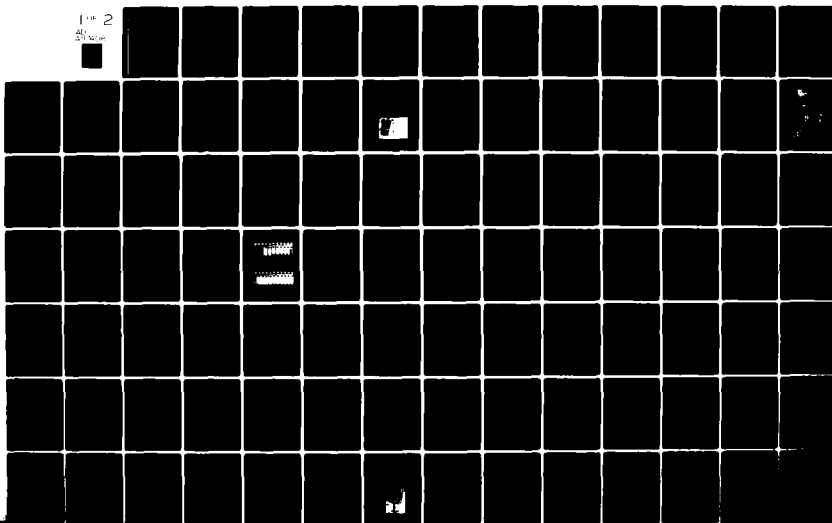
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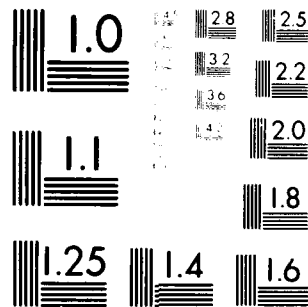
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RESEARCH ON FIRE-RESISTANT DIESEL FUEL

INTERIM REPORT
AFLRL No. 145

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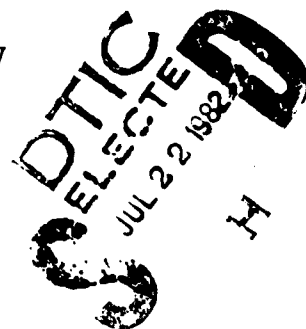
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20. ABSTRACT (Cont'd)

used in FRF formulations. DF-2, DF-1, DF-A, and NATO diesel fuel samples were obtained from refineries, bulk storage, and service stations. Aromatic concentrate (AC) products from various sources were evaluated for use in adjusting the total aromatic ring carbon (TARC) content of FRF formulations. Neat base fuel and AC-containing base fuel TARC effects on microemulsification efficacy were established for water containing various amounts of total dissolved solids and for the amide/amine/soap emulsifier with various levels of total acid number.

No phase stability problems were encountered when FRF was blended at various temperatures between 0° and 50°C or subjected to cycling between 2° and 50°C. Six-month storage stability tests were conducted at temperatures between 4° and 40°C. Phase separation occurred after one month at 40°C, but all other FRF samples survived. Corrosion tests confirmed that iron is protected from corrosion by FRF and that an aryltriazole additive inhibits corrosion of copper and its alloys.

Some FRF formulations exhibited anomalously high viscosities at ambient and/or reduced temperatures. When these were observed, they also decreased with the sample age. Dilution of FRF with other base fuels or addition of various diesel fuel additives, such as antioxidants and cetane number improvers, did not cause adverse effects on phase stability. Low-temperature studies in a simulated DD 6V-53T diesel engine fuel system demonstrated cavitation caused by filter plugging on the suction side of the fuel pump at fuel temperatures below 0°C, with and without the use of anti-icing or flow-improver additives.

A spectral absorbance method was defined for the objective evaluation of FRF microemulsion appearance. Dielectric constant measurements of FRF blends indicated that, for the excitation frequencies used in this study, this property changed with time and was relatively insensitive to FRF water content.

As part of a basic research study of FRF self-extinguishing mechanisms, vapor pressure measurements revealed a strong liquid-phase water concentration dependence for the equilibrium partial pressure of water and indicated a transition in phase behavior as the water content of the liquid is decreased below 5 vol%, suggesting a transition from microemulsions to micellar solutions. Measured flammability limits of diesel fuel vapor/water vapor mixtures and measured vapor pressure data correlated quantitatively with the observation that pool flame propagation occurred only when the liquid phase water content was less than 1 vol% and with the maximum observable flash point for FRF of 67°C.

A NATO-cycle endurance test of FRF was conducted by the U.S. Army Tank Automotive Command (TACOM). During 168 hours of operation with an AVDS-1790-2C diesel engine, two nonfuel-related mechanical failures occurred, the last one terminating the test. Inspection of engine parts from the undamaged side of the engine established that no abnormal fuel-related distress was evident. A continuous blending system was obtained and modified by this laboratory, and it was used by TACOM to prepare the FRF for this test.

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EXECUTIVE SUMMARY

Engine recycle effects on physical and fire-vulnerability properties of fire-resistant diesel fuels, FRF and FRF-B (without and with antimist agent, respectively), were determined using the 6V-53T engine and the AFLRL 20-mm High-Explosive Incendiary Tracer (HEIT) ballistic test. Results showed that recycled FRF-B offers no advantages in fire vulnerability reduction relative to FRF; also, the recycled FRF appeared unchanged while the misting properties of the recycled FRF-B had been degraded to the equivalent of those of FRF. Accordingly, investigation of FRF-B was terminated.

During this program, 33 different base fuels, including DF-2, DF-1, DF-A, and NATO F-54 types, have been used in the characterization of FRF formulations. Selected properties, such as distillation range, density, flash point, total aromatics, and total aromatic ring carbon (TARC) content have been evaluated for all of these fuels. All specification-type properties were determined on several selected fuels. The efficacy of the previously selected amide/amine/soap emulsifying agent has been further evaluated at three levels of total acid number (TAN). Aromatic concentrate (AC) samples from various sources have been evaluated for use in increasing the TARC of FRF blends. These concentrates, which contain 100 percent aromatic compounds, are typically produced as the heavy residue, C_9^+ , in the manufacture of benzene, toluene, and xylene (BTX bottoms).

FRF formulation composition "windows" for "no-failure" microemulsification have been established for water compositions ranging from 0 to 500 ppm total dissolved solids (TDS) and base fuel compositions ranging from 15 to 25 wt% total aromatic ring carbon. Low total acid number surfactants are most effective with low TDS water and vice versa. Low TARC base fuels require low TAN surfactants and vice versa.

FRF was made at various temperatures between 0° to 50°C. At the time of blending, some compositions were macroemulsions at 0°C. However, when they were allowed to warm to ambient temperature, they turned into microemulsions. No phase stability problems surfaced under any of these experimental conditions.

The visual appearance of FRF microemulsions with various surfactant concentrations was documented by photographs, and the droplet size distribution in such blends was evaluated by photon correlation spectroscopy. The average droplet diameter increased from about 100 to 200 Å as the surfactant content was decreased from 10 to 5 vol%, respectively.

Six-months storage stability was evaluated on FRF compositions based upon two diesel fuels. Samples were stored under ambient conditions and at constant temperatures of 4°, 24°, and 40°C. At 40°C, the FRF survived for one month only; under the other conditions, all fuels survived without ill effects for the full test period.

FRF formulations made with several base fuels and two water compositions were subjected to cycling between 50° and 2° C six times. All samples survived these cycling experiments.

Corrosion tests were performed on FRF blends based upon two different base fuels using San Antonio tap water, containing approximately 300 ppm of total dissolved solids. Tolyltriazole corrosion inhibitor was predissolved in the appropriate surfactant to yield inhibitor concentrations of 500 and 1000 ppm in the final FRF blends. Copper and two different brass alloy specimens were partially immersed in the test fluids, and each specimen was placed in an oven at 55°C for 100 and 200 hours. The highest values of weight losses were observed in the uninhibited FRFs. These weight losses were reduced, but were not completely eliminated by the inhibitor.

Viscosity measurements revealed that some FRF blends exhibit anomalously high viscosities at 10°C and lower temperatures, while behaving normally at 15°C and higher temperatures. When such anomalous viscosities occur, they also decrease with time. The significance of these results relative to field use of FRF is yet to be established.

Dilution experiments with three different base fuels indicated that no phase stability problems should be encountered upon mixing of FRF blends with other base fuels.

Various diesel fuel additives, such as antioxidants and cetane number improvers, were investigated. No adverse effects on FRF phase stability were observed.

No problems with FRF phase stability which could be attributed to base fuel contamination have been encountered during this program. Moreover, special FRF formulations, in which up to 1000 ppm of standard dust was included, showed no adverse effects of the dust on phase stability.

A modified liquid-solid separator (referred to herein as the Frozen Fuel Detector) with an in-depth type sintered metal filter was successfully used to separate solids from FRF at low temperatures. The device was used to investigate the effects of wax crystal modifiers on low-temperature filterability of typical FRF compositions. Results appeared promising for pressurized flow through the filter at subzero ($^{\circ}\text{C}$) temperatures. A simulated DD6V-53T fuel system contained in a low-temperature chamber experienced cavitation caused by filter plugging on the suction side of the fuel pump at all filter temperatures below 0°C . This problem was not alleviated by the use of anti-icing or flow-improver additives.

A spectral absorbance method has been defined for the objective determination of the quality of FRF formulations as indicated by their appearance. This method could be employed in the field by diverting a side stream of blended FRF through a pass/fail black box which detects the absorbance of a narrow band of visible radiation (e.g., ca. 550 nm wavelength).

Extensive measurements were made of the dielectric constant of FRF formulations of varying water content. The results indicated that this property changes with time and, for the excitation frequencies used in this study, is relatively insensitive to water content in the 9 to 11 vol% water concentration range. Field methods for determining water content remain a problem.

A new phase of the Army's FRF development program was initiated with the objective being to conduct basic research on the influences of fire-resistant fuel composition, physical properties, flammability properties, and imposed conditions on the mechanisms of flammability mitigation which func-

tion in such fuels. The first area selected for study was the dilution effect of water vapor in suppressing the flammability of combustible fuel/air mixtures. An experimental apparatus was assembled to measure the effect of water vapor dilution on the flammability of hydrocarbon/air mixtures. The flammability limits apparatus was calibrated with isooctane, and flammability measurements on diesel fuel vapor/water/air mixtures were completed for three different flash point fuels (72°, 60°, and 45°C). The apparatus for measuring flammability limits was modified to accommodate the precise measurement of vapor pressure to determine if water-in-fuel microemulsions are truly immiscible systems. Vapor pressure measurements were made on the neat diesel fuel, water, and two microemulsions, each containing 6 percent surfactant with 10, 5, 1 and 0.5 percent water, respectively. Pool flammability experiments were also conducted. Results of the vapor pressure studies reveal a strong liquid phase water concentration dependence of the water vapor partial pressure, contrary to the behavior of truly immiscible aqueous macroemulsions. The results also indicate a transition in phase behavior as the water content is decreased to less than 5 vol%, suggesting a transition from microemulsions to micellar solutions at the lower water concentrations. Peak flammability results measured for diesel fuel vapors, when considered in light of the vapor pressure data, correlate quantitatively with the observation that pool flame propagation occurs when the liquid phase water content is less than 1 vol%.

Liaison was maintained with the U.S. Army Tank and Automotive Command (TACOM) project officer for the AVDS-1790 FRF endurance test. AFLRL defined the surfactant requirements, and confirmed that the surfactant purchased for the endurance test would produce satisfactory microemulsions with the VV-F-800 diesel fuel purchased for the test, using either deionized water or tap water (San Antonio or Detroit). In a NATO-cycle endurance test of FRF, 168 hours were completed in a full-scale AVDS-1790-2C engine. Two nonfuel-related mechanical failures were encountered, the second one leading to test termination. Inspection of engine parts from the undamaged side of the engine was conducted by an experienced rater from AFLRL. No abnormal fuel-related distress was evident. A continuous blending system was obtained and modified by AFLRL, and it was used by TACOM for preparing FRF for this test.

FOREWORD

This report was prepared at the U.S. Army Fuels and Lubricant Research Laboratory (AFLRL), Southwest Research Institute, under DOD Contract Nos. DAAK70-80-C-0001 and DAAK70-82-C-0001. The project was administered by the Fuels and Lubricants Division, U.S. Army Mobility Equipment Research and Development Command (MERADCOM), Fort Belvoir, Virginia 22060, with Mr. F. W. Schaekel, DRDME-GL, serving as Contracting Officer's Representative. This report covers the period of performance from 1 October 1979 to 31 December 1981.

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I. INTRODUCTION

Background

Development of water-in-middle distillate diesel fuels as "fire-resistant fuels" (FRF) was first comprehensively reported in 1979. (1)* It was shown that a clear to hazy aqueous diesel fuel microemulsion could be prepared that exhibits diminished mist flammability with self-extinguishing pool fires, even at temperatures well above the flash point of the base fuel. No difficulties were encountered in starting, idling, and running unmodified diesel engines on such fuels.

In this report, further developments are described with major emphasis on establishing realistic compositional requirements for base fuels, surfactants, and water, and on the analysis of the resultant microemulsion.

Objectives of Continuing Investigation

The objective of these studies is to assure optimum performance and maximum reliability of field-blended fire-resistant diesel fuels for use in diesel or gas turbine powered Army equipment.

The FRF research conducted during this report period has included basic studies, exploratory development, and advanced development investigations. This continuing research effort is summarized schematically in Figure 1.

II. EXPLORATORY DEVELOPMENT RESEARCH

The need continues for the development of fuels for Army combat/mobility equipment which are capable of yielding reduced fire vulnerability hazards. Toward this end, exploratory development research has been conducted in various areas important to the eventual field use of fire-resistant diesel fuel (FRF) as a combat fuel.

* Underscored numbers in parentheses refer to the list of references at the end of this report.

Antimist Fire-Resistant Diesel Fuel Degradation

The initial objective of the exploratory development research was to provide sufficient experimental data to allow a decision as to whether the reduced-water-content antimist candidate fire-resistant diesel fuel (FRF-B) should be further investigated. To determine the effects of fuel system recycle on FRF properties, 300-gallon blends of both FRF (10 vol% water and 6 vol% surfactant) and FRF-B (5 vol% water, 3 vol% surfactant, and 0.2 wt% AM-1) were prepared. A DD6V-53T diesel engine was operated with each fuel blend until 250 gallons had been consumed. The fuel was drawn from and recycle returned to a special 400-gallon tank located outside of the engine cell as shown in Figure 2. The 50 gallons remaining after the engine run were used in comparative evaluations with virgin blends of the same formulation. The results of the engine tests, of AFLRL 20-mm High Explosive Incendiary Tracer (HEIT) ballistic tests, and laboratory inspection tests are presented in Table 1. These results are summarized as follows:

- Incompatibility with fuel pump suction side filter (cavitation) was observed with FRF-B. No such problems were encountered with FRF.
- The maximum power obtained with FRF was less than that observed with base fuel because of the lower heat of combustion. The same was true for FRF-B, but additional power loss was observed with FRF-B and was attributed to fuel system difficulties in handling the thickened fuel. Maximum power was obtained during the FRF-B test after significant antimist polymer degradation had occurred.
- Fuel system recycling had no effect on FRF in terms of either phase degradation or changes in flammability characteristics.
- Substantial antimist quality degradation did occur in FRF-B blends during recycle. These results were confirmed by viscosity measurements and by ballistic evaluations in which the mist fireball was equivalent to that observed with neat DF-2. Pool-burning self-extinguishment did occur with recycled FRF-B, but it was delayed relative to that observed with recycled FRF.

TABLE 1. RESULTS OF FRF ENGINE DEGRADATION STUDIES

Fuel	Measured Water vol %	Antimist Agent Content wt% AM-1	Relative Kinematic Viscosity at 40°C	Relative Maximum Engine Load at 2800 rpm	20-mm Ballistic Test Results
DF-2 Base Fuel	0.0	0.0	1.0	1.0	Large transient fireball, full pool burning.
FRF-B (Start of Test)	5.0	0.2	3.5	0.8	Small transient fireball, no residual pool burning.
FRF-B (End of Test)	4.3	---	1.5	0.9	Large transient fireball, self-extinguishing pool burning.
FRF (Start of Test)	9.7	0.0	1.7	0.9	Large fireball, no residual pool burning.
FRF (End of Test)	9.4	0.0	1.7	0.9	Large fireball, no residual pool burning.

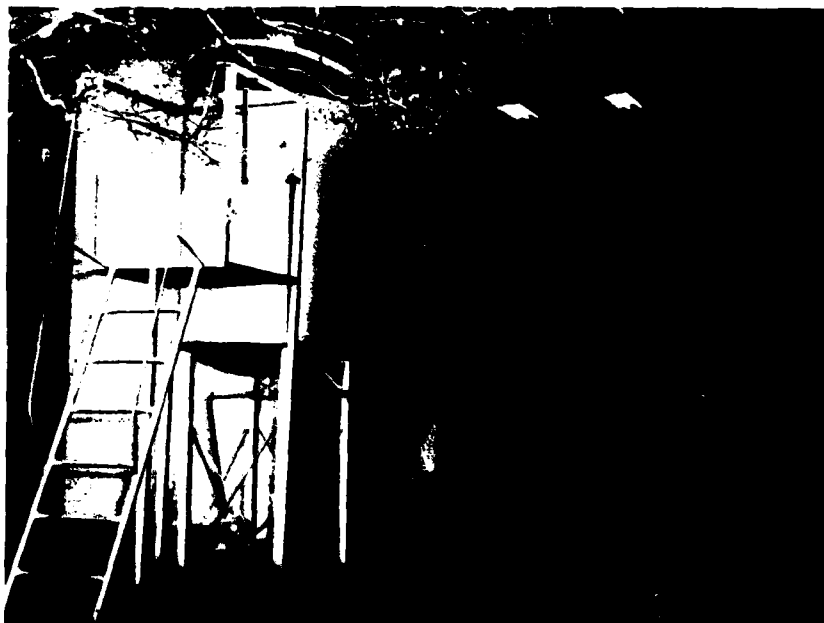


FIGURE 2. 400-GALLON SUPPLY AND RECYCLE TANK FOR DD6V-53T ENGINE TEST CELL

- Because of these results, further investigation of FRF-B was suspended.

Fire-Resistant Diesel Fuel Formulation Characterization

The FRF microemulsion formation selected for exploratory and advanced development research nominally comprises diesel fuel, emulsifying agent, and water at volumetric concentrations of 84, 6, and 10 percent, respectively.

Base Fuels:

Two different base fuels have been used as reference fuels in this research, and their properties are summarized in Table 2. In addition to these, other base fuels were obtained from refineries, service stations, and from domestic military and European NATO installations. While "full" petroleum laboratory analysis was performed on most of these fuels, only density, distillation data, flash point, and two measures of aromatic character are reported in Table 3. Table 4 lists more extensive analyses of the NATO F-54 fuel samples. Aromatic ring carbon content was shown to correlate best (but not exclusively) with their emulsifiability, as is discussed in a later section of this report. One of these methods measures the aromatic hydrocarbon content by high-performance liquid chromatography (HPLC).⁽²⁾ By this method, any hydrocarbon with an aromatic ring will register as an aromatic hydrocarbon. The other method measures the quantity of carbon atoms within aromatic ring structures by ultraviolet spectroscopy.⁽³⁾ An approximate empirical relationship between the HPLC and UV determined data was derived as illustrated by Figure 3.

$$\text{Aromatic Hydrocarbons by HPLC} = 1.4(\text{TARC}) + 4.8$$

where TARC is the Total Aromatic Ring Carbon content, wt%, as determined by UV.

These two methods measure related, but nonidentical properties; each is correct within its defined limits. As shown later, the fuels' total aromatic ring carbon (TARC) content more closely describes its suitability for microemulsification.

TABLE 2. PROPERTIES OF REFERENCE DIESEL FUELS

Property	No. 7225	No. 8821
Specification Type	MIL-F-46162A(MR)-II	Fed. Spec. VV-F-800b-DF-2
Gravity, °API at 15.5°C	36.1	35.2
Density, g/mL at 15.5°C	0.844	0.848
Flash Point, PMCC, °C(°F)	60 (140)	72 (161)
Fire Point, °C(°F)	91 (196)	84 (183)
Cloud Point, °C(°F)	-21 (-6)	-1 (30)
Pour Point, °C(°F)	-24 (-11)	-10 (14)
Kinematic Viscosity, cSt at 40°C	2.2	3.2
Accelerated Stability		
(ASTM D 2274), mg/100 mL	0.6	2.7
Total Acid No., mg KOH/g	0.01	0.03
Steam Jet Gum, mg/100 mL	3.9	3.2
Sulfur, wt%	0.35	0.47
Copper Strip Corrosion		
(ASTM D 130)	1A	1A
Carbon, wt%	86.8	86.7
Hydrogen, wt%	13.2	13.3
Heat of Combustion (Gross), J/kg	45.1 x 10 ⁶	45.7 x 10 ⁶
(Btu/lb)	(19,427)	(19,670)
Heat of Combustion (Net), J/kg	42.5 x 10 ⁶	42.8 x 10 ⁶
(Btu/lb)	(18,283)	(18,450)
Hydrocarbon Types,		
FIA, vol% saturates	---	69.1
aromatics	---	29.4
Hydrocarbon Types,		
HPLC, wt% saturates	72.5	74.1
aromatics	27.5	25.9
Aromatic Ring Carbon,		
UV, wt% mononuclear	7.08	7.50
dinuclear	11.47	6.54
trinuclear	0.31	0.36
total	18.86	14.40
Cetane No.	48	51
Distillation (ASTM D 86), °C(°F)		
Initial Boiling Point	166 (331)	183 (362)
10% Distilled	219 (426)	225 (437)
50% Distilled	244 (471)	282 (539)
90% Distilled	296 (565)	331 (628)
End Point	358 (676)	361 (682)

TABLE 3. ANALYSES OF BASE FUELS

Serial No.	Fuel Code No.	Source	Density, g/mL at 15.5°C	Distillation ASTM D 86, °C				Aromaticity wt% by HPLC	Aromatic Ring Carbon wt% by UV			Flash Pt, °C (PMCC)		
				IBP	10%	50%	90%		EP	Mononuclear	Dinuclear		Trinuclear	TARC
1	7225	Refinery	0.8438	166	218	244	294	358	27.5	7.08	11.47	0.31	18.86	61
2	7896	Refinery	0.8499	173	207	256	298	330	29.4	10.94	5.54	0.14	16.62	67
3	7907	Serv. Station	0.8479	188	219	266	312	339	29.0	9.69	8.05	0.4	18.15	63
4	7908	Serv. Station	0.8369	184	222	263	311	336	31.5	9.00	9.45	0.47	18.92	54
5	7909	Serv. Station	0.8504	204	240	273	331	367	26.1	7.43	8.68	0.30	16.41	76
6	7910	Serv. Station	0.8454	206	237	276	316	332	24.8	9.77	4.14	0.17	14.08	77
7	7911	Serv. Station	0.8423	194	219	261	319	354	23.6	7.91	6.19	0.24	14.34	74
8	7812	Serv. Station	0.8369	196	227	276	331	359	19.7	8.05	4.66	0.24	12.95	65
9	7817	Refinery	0.8388	187	203	238	309	336	20.9	9.86	4.23	0.13	14.22	66
10	7831	Refinery	0.8556	223	231	264	306	337	35.5	11.67	10.59	0.54	22.80	88
11	7996	Refinery	0.8479	183	221	263	310	333	39.5	8.75	9.73	0.42	18.90	68
12	8445	Refinery (Special)	0.8698	184	219	263	316	363	45.1	12.84	12.24	1.11	26.19	75
13	8652	NATO F-54	0.8354	182	220	266	312	342	21.4	7.67	4.69	0.20	12.55	66
14	8821	Refinery	0.8484	183	225	282	331	361	25.9	7.50	6.54	0.36	14.40	72
15	9294	Refinery (DF-1)	0.8142	212	219	229	278	325	----	3.40	6.70	0.10	10.20	---
16	9354	Refinery (DFA)	0.7893	166	179	192	214	247	----	5.50	2.40	0.00	7.90	---
17	10135	TACOM	0.8535	186	220	258	302	338	33.4	9.70	10.60	0.60	20.90	61
18	10191	Serv. Station	0.8436	176	220	268	312	359	24.5	8.21	5.60	0.20	14.01	---
19	10192	Serv. Station	0.8487	174	212	269	307	337	31.9	9.73	7.10	0.30	17.19	---
20	10193	Serv. Station	0.8620	185	229	277	322	349	28.8	9.21	5.47	0.20	14.93	---
21	10194	Serv. Station	0.8378	193	223	264	311	345	22.5	8.58	5.14	0.18	13.90	---
22	10195	Serv. Station	0.8557	195	236	279	337	376	23.5	7.52	5.91	0.24	13.67	---
23	10196	Serv. Station	0.8398	184	218	263	312	357	23.0	8.00	5.06	0.18	13.24	---
24	10197	Serv. Station	0.8447	181	221	261	303	339	24.8	9.96	6.62	0.19	16.77	---
25	10198	Serv. Station	0.8357	171	212	260	314	348	23.9	8.71	4.63	0.18	13.52	---
26	10199	Serv. Station	0.8542	186	233	279	340	368	20.9	6.91	5.62	0.23	12.76	---
27	10200	Serv. Station	0.8388	179	218	267	324	356	24.9	8.91	4.87	0.22	14.00	---
28	10713	NATO F-54	0.8343	180	210	261	314	329	26.1	8.19	4.39	0.19	12.77	66
29	10714	NATO F-54	0.8222	168	191	233	318	347	23.7	8.67	3.27	0.14	12.08	57
30	10924	NATO F-54	0.8275	191	211	244	314	346	20.9	8.79	3.07	0.09	11.96	73
31	11014	NATO F-54	0.8393	196	227	266	315	353	25.3	6.88	5.62	0.26	12.76	76
32	11015	NATO F-54	0.8275	174	211	254	316	341	23.3	7.08	4.69	0.18	11.95	57
33	11016	NATO F-54	0.8165	177	199	245	316	347	25.0	8.89	4.10	0.19	13.18	62

TABLE 4. PROPERTIES OF NATO F-54 FUELS

Code No.: Description	Test Method ASTM D	Properties	VV-F-800C DF-2: OCONUS F-54 Requirements	8652 MERADCOM F-54	10713 Shell Permls F-54	10714 Esso Rotterdam F-54	10924 Pump Station Engden	11014 Shell F-54	11015 CFR F-54	11016 SRS/BP/DOL F-54
Density, kg/L @ 15°C	287		0.815 to 0.860	0.8353	0.8343	0.8222	0.8275	0.8383	0.8275	0.8165
Flash Point, °C	93		58 min	66	66	57	73	76	57	62
Cloud Point, °C	2500		-13 max	ND	-4	-5	-5	-13	-12	-8
Pour Point, °C	97		-18	ND	-18	-24	-18	-18	-21	-21
K vis @ 0°C, cSt	445		-	ND	ND	ND	5.78	5.95	6.53	5.12
K vis @ 20°C, cSt	445		1.8 to 9.5	ND	3.87	2.93	3.45	4.41	3.75	3.13
K vis @ 40°C, cSt	445		-	2.60	2.51	1.98	2.27	2.78	2.44	2.10
Distillation, °C	86									
IBP			-	182	180	168	191	196	174	177
10% recovered			-	220	210	191	211	227	211	199
50% recovered			Report	266	261	233	244	266	254	245
90% recovered			357 max	312	314	318	313	315	316	316
EP			370 max	342	329	347	345	353	340	347
Residue, vol%			3 max	1.5	3	2	1.5	1.5	1.8	1.5
Carbon Residue on										
10% bottoms, mass%	524		0.20 max	ND	0.09	0.08	0.08	0.09	0.05	0.05
Sulfur, mass%	(XRF)		0.70 max	0.44	0.22	0.14	0.13	0.50	0.08	0.35
Copper Strip Corrosion										
3 hr @ 50°C, rating	130		1 max	1a	1a	1a	1a	1a	1a	1a
Ash, mass%	482		0.02 max	ND	0	0	0	0.01	0	0
Accelerated Stability										
Total Insolubles,										
mg/100 ml	2274		1.5 max	ND	ND	ND	0.76*	5.8*	0.42*	ND
Neutralization Number										
TAN, mg KOH/g	664		0.10 max	ND	0.04	0.02	0.01	0.03	0.01	0.01
Particulate Contamina-										
tion, mg/100 mL										
Cetane Number	613		10 max	ND	ND	ND	1.6*	13.5*	1.3*	ND
Existent Gum, mg/100 ml	381		45 min	52	48	47	52	53	54	54
Aromatics, wt%, by HPLC	-		-	0.22	2.2	1.0	0.5	5.5	0.9	0.4
Aromatic Ring Carbon,				21.4	26.1	23.7	20.9	25.3	23.3	25.0
wt%, by UV										
mononuclear	-		-	7.67	8.19	8.67	8.79	6.88	7.08	8.89
dinuclear				4.69	4.39	3.27	3.07	5.62	4.69	4.10
trinuclear				0.20	0.19	0.14	0.09	0.26	0.18	0.19
total (TARC)				12.56	12.77	12.08	11.96	12.76	11.95	13.18

ND = not determined; sample consumed in other tests.

* = Determined on smaller than normal size sample.

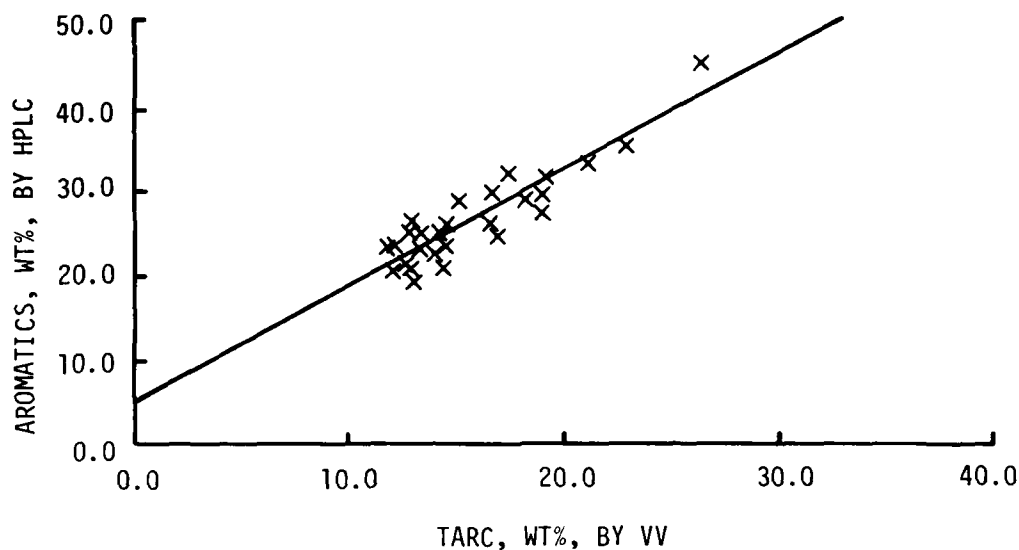
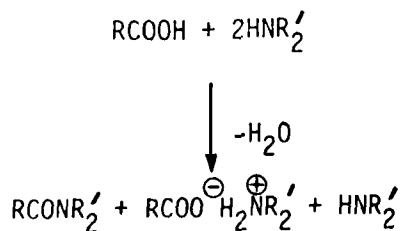


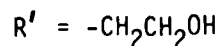
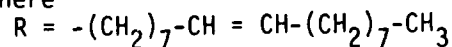
FIGURE 3. CORRELATION BETWEEN TOTAL AROMATICS CONTENT AND TOTAL AROMATIC RING CARBON (TARC) CONTENT OF FRF BASE FUELS

Surfactant Mixture:

Emulsifying Agent -- The emulsifying agent (EA) used for the microemulsification of water in diesel fuels was previously selected from a large number of ashless, sugar-free (i.e., nondepositing) candidate compositions. (1) This selected EA is synthesized commercially at elevated temperatures under reduced pressure by reacting one mole of oleic acid with two moles of diethanolamine to form oleyl diethanolamide and diethanolamineoleate soap according to the scheme:



where



Molecular models of the amide, amine, and water are shown in Figure 4.

These "two-to-one," or "Kritchevsky amides" contain less ester-type byproducts than those made by the reaction between equimolar amounts of carboxylic acid and diethanolamine.(4,5) As discussed in later portions of this report, modification of the commercially available EA is necessary in the case of certain base fuels and when "hard" water is used. The modification of the EA consisted of enhancing its hydrophilic character by increasing its soap content. This step was accomplished by reacting part of the product's excess diethanolamine with additional amounts of oleic acid.

Impurity Identification -- Commercially available oleic acid is not pure oleic acid. Even a "USP" grade product contains only about 76 percent of oleic acid. The balance of the composition--according to gas-liquid chromatography--includes saturated carboxylic acids (lauric-, myristic-, pentadecanoic-, palmitic-, heptadecanoic-, and stearic acids), mono-unsaturated acids (e.g., tetradecenoic-, and palmitoleic acids) and polyunsaturated acids (e.g., linoleic- and linolenic acids.)

In this project, the surfactant performance as a function of fatty acid distribution was not studied because of the chemical complexity of the system, and because no commercial surfactant is available (or feasible) that is based upon pure oleic acid.

A crystalline material has separated from some of the commercially obtained oleyl diethanolamide surfactants. This product's presence is deleterious to FRF formation. It became important to determine the identity and source of this material. The crystals were isolated, washed with heptane, and recrystallized from warm methylene chloride or warm chloroform. This product is water soluble and has a sharp melting point of 136° to 137°C. Proton nuclear magnetic resonance at 90 MHz in deuterated chloroform (CDCl_3) exhibited only four absorbances in the 10-ppm sweep between $\delta 0.0$ and $\delta 10.0$:

- (a) δ 2.58 singlet
- (b) δ 2.58 triplet underlying above singlet, $J=5.2$ Hz
- (c) δ 2.75 singlet, slightly broad, "exchangeable proton"
- (d) δ 3.76 triplet, $J=5.2$ Hz

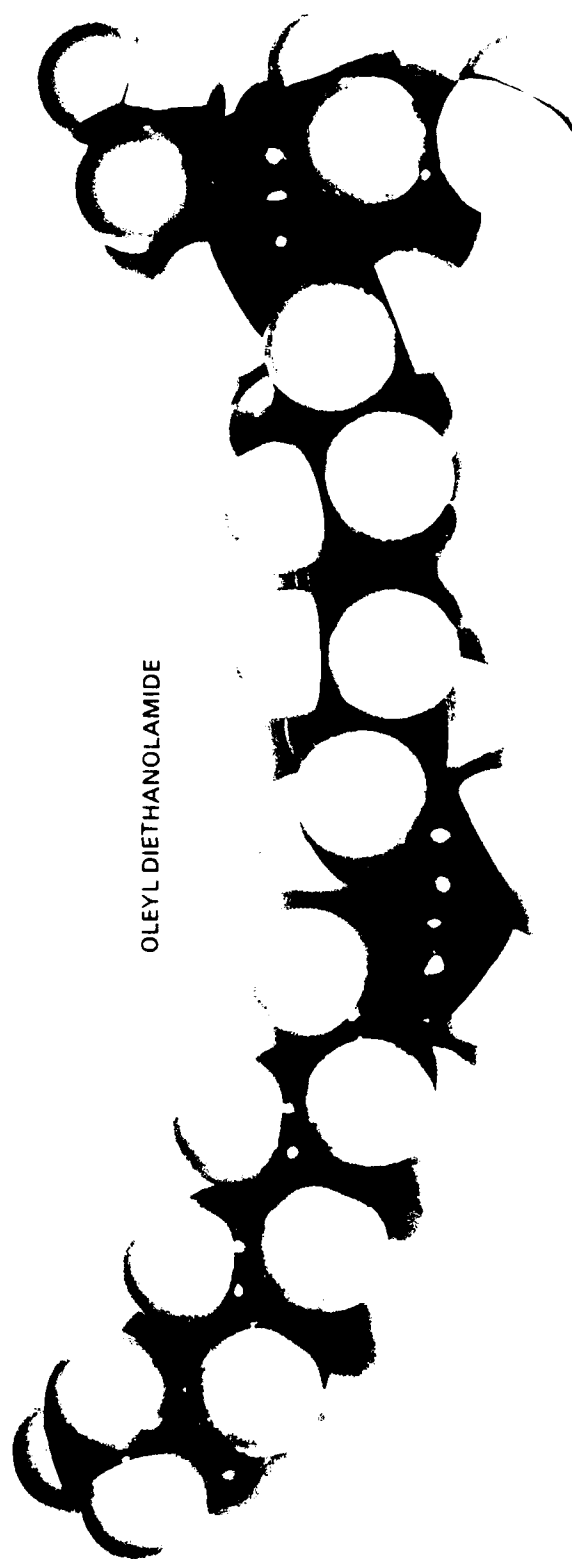
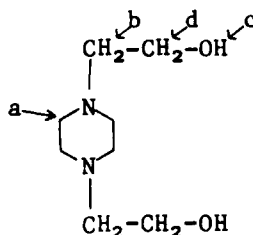


FIGURE 4. STUART MOLECULAR MODELS OF THE MAJOR CONSTITUENTS OF THE FRF SURFACTANT MIXTURE AND WATER

This ^1H -NMR spectrum and its integrated values are consistent with that expected of N,N-di(2-hydroxyethyl)-1,4-piperazine (may also be named 1,4-piperazinediethanol), according to the following assignments:



Infrared analysis in a KBr pellet is also consistent with this structural assignment, exhibiting a broad peak centered at 3140 cm^{-1} ($3.18\text{ }\mu\text{m}$) indicative of a highly hydrogen-bonded structure. In chloroform solution, this IR band shifts to the expected frequency of 3450 cm^{-1} ($2.9\text{ }\mu\text{m}$). The product's melting point of 136° to 137°C is in good agreement with literature data (6,7,8) and is also indicating a highly associated molecular structure. Elemental analysis is:

	Calculated for $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_2$	Found
Carbon, wt%	58.15	54.6
Hydrogen, wt%	10.41	10.8
Nitrogen, wt%	16.08	---
Oxygen, wt%	18.36	---

It was concluded that this compound was made during either the synthesis of the diethanolamine or the surfactant by the self-condensation of diethanolamine and did not stem from extraneous contamination. Avoidance of this contaminant must be the responsibility of the surfactant manufacturer.

Aromatic Concentrate -- Recently, the concentration of aromatics in diesel fuels has been lowered by refiners. This lower concentration may render some of these fuels unsuitable for FRF production due to incompatibility

with the emulsifying agent. For such cases, it becomes desirable to increase the aromatic character of the base diesel fuel by the addition of an "aromatic concentrate" (AC), or "BTX-bottoms" (C_9+ Aromatics).

Extensive analyses were made on the initial batch of aromatic concentrate (BTX bottoms), and these are presented in Table 5. Abbreviated analyses of subsequent batches obtained from various suppliers are summarized in Table 6. The effects of added aromatic concentrate on the flash point and cetane number of FRF blends made from several different base fuels were evaluated, and these results are listed in Table 7.

It was found that, in most instances, replacement of 6 vol% of the base fuel by the same amount of AC will yield a microemulsion. Since the AC is a good solvent for the highly viscous emulsifying agent (kinematic viscosity at 20°C is approximately 1900 cSt), and because normally both are used at 6 vol% concentration, a 1:1 (by volume) surfactant solution may be made in AC, and this lowered-viscosity surfactant solution (kinematic viscosity at 20°C approximately 40 cSt) may be added to 78 volume parts of the base fuel. This composition will normally allow the microemulsification of 10 volume parts of water.

Emulsification With Special Additives--Attempts were made to alleviate the emulsion destabilizing effects of electrolytes, mainly Ca^{2+} and Mg^{2+} , in tap water, so that one surfactant with a specific TAN could be used to microemulsify essentially any water (with TDS of up to 300 or 500 ppm) in any diesel fuel.

In this study the TAN of oleyl diethanolamide-diethanolamine surfactant was adjusted to 15.5, and 19.0 mg KOH/g, and FRF blends were made with both in a large number of base fuels. The water in these blends contained up to 500 ppm of calcium nitrate as the electrolyte, chelating agents di- and tetra-sodium and di- and tetra-ammonium salts of ethylenediaminetetraacetic acid [Na_2EDTA , Na_4EDTA , $(NH_4)_2EDTA$, and $(NH_4)_4EDTA$] were used at 200 and 1000 ppm concentrations. Under the investigated conditions, none of the four chelating agents produced desirable effects.

Some earlier results in this program suggested that addition of high molecular weight polyalphaolefins ($MW \approx 5 \times 10^6$) in specific instances improved microemulsification of water in diesel fuels, possibly through the formation of a protective colloid structure. Compositional requirements to achieve such beneficial results in all instances could not be established. Addition of 0.1 to 0.2 wt% of polyalphaolefins of lower molecular weight (2.8×10^6 ; 1.7×10^6 ; 1.0×10^6), or a proprietary "fuel oil wax crystal modifier" ($MW \approx 6500$) either did not affect microemulsification, or their presence was deleterious.

FRF Composition Limits:

Compositional limits were determined for "no-failure" FRF production in terms of the total aromatic ring carbon (TARC) content (2) of the fuel component, the total dissolved solids (TDS) content of the water and the total acid number (TAN) of the surfactant, expressed as mg KOH per gram of sample. The TAN value of the oleyl diethanolamide-diethanolamine surfactant has been adjusted by addition of oleic acid to 15.5, 17.1, and 19.0 mg KOH/g, corresponding to surfactant numbers EA-78, EA-97, and EA-90, respectively. Using the 33 distillate fuels listed in Table 3, emulsification was attempted with 6 vol% of each of these surfactants using 10 vol% water containing 50, 100, 300, and 500 ppm of calcium nitrate as the total dissolved solids (TDS) component. Figures 5a through 5c portray the individual data points obtained, together with the bracketing conditions within which each blend yielded a stable microemulsion. In these figures, the 33 different base fuels are plotted as the abscissa, using their serial numbers from Table 3, in duplex graphs--with and without AC. Stable microemulsions are indicated by solid dots and macroemulsions and unstable emulsions as open circles. These brackets are summarized in Table 8.

The conditions of TDS and TARC which bracket the "windows" for no-failure are summarized in Table 8. Two apparent "rules of thumb" are suggested by these data. The first is that low TAN surfactants (ca. 15 mg KOH/g) are effective for forming microemulsions with low electrolyte content (low TDS)

water (e.g., 0 to 100 ppm TDS). Conversely, high TAN surfactants (ca. 19 mg KOH/g) may microemulsify high TDS water (e.g., up to 500 ppm TDS), albeit with more restrictive base fuel TARC values. The additional "rule of thumb" is that, for all water and surfactant compositions studies, minimum base fuel TARC required for microemulsification (wt%) is approximately numerically equal to the TAN of the surfactant (mg KOH/g). However, in the case of the lowest TAN surfactant, when 6 vol% of aromatic concentrate is added to the formulation, the minimum TARC (including the contribution of the added AC) is reduced to about 12.

An alternate and more general presentation of these data is given in Tables 9a, b, and c. Additionally, those compositions yielding stable microemulsions (i.e., ratings of 1, 1T, 2, or 2T) are correlated with water composition in Figures 6a, b, and c, and those yielding stable micro- or macroemulsions (i.e., ratings of 1, 1T, 2, 2T, 3, 3T, or 4) are portrayed in Figures 7a, b, and c. In all of the cases represented by these figures, substitution of AC for 6 vol% of the base fuel in the formulation, favored the formation of stable emulsions. Moreover, these graphs illustrate that, irrespective of the base fuel TARC, successful emulsification with the low TAN surfactant is favored by use of 6 vol% AC and use of water of low TDS content. Similarly, they indicate that the percentage of base fuels yielding stable emulsions is least sensitive to the water TDS when using the intermediate TAN surfactant. Both the low TAN and the high TAN surfactants give consistently high yields of stable emulsions only over rather narrow ranges of water TDS, whereas the intermediate TAN surfactant gives consistent, but slightly lower, yields of stable emulsions over a broad range of water TDS.

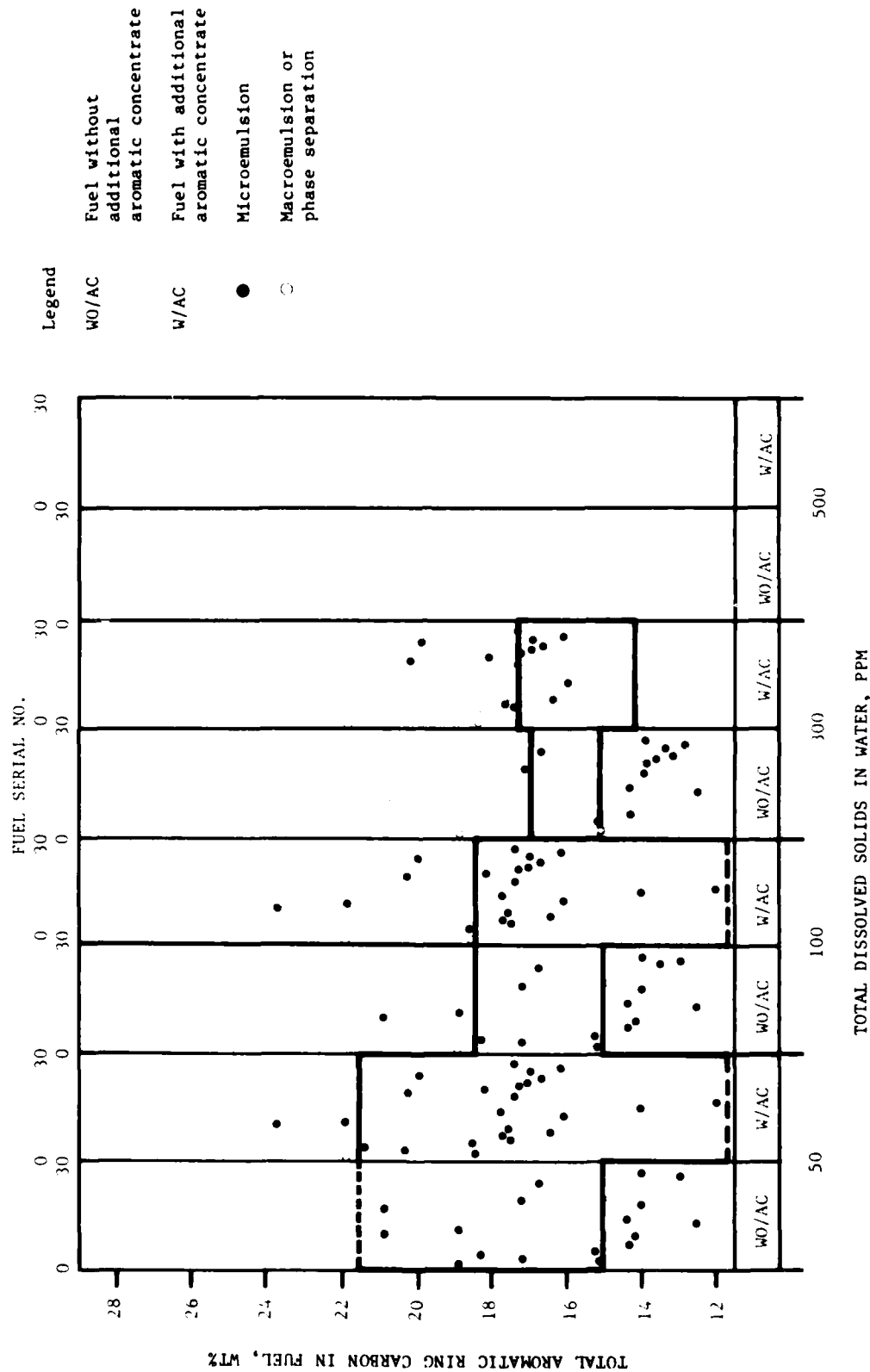


FIGURE 5a. INTERACTIONS BETWEEN FUEL TARC AND WATER TDS IN VARIOUS FUELS USING EA-78 (TAN = 15.5 mg KOH/g)

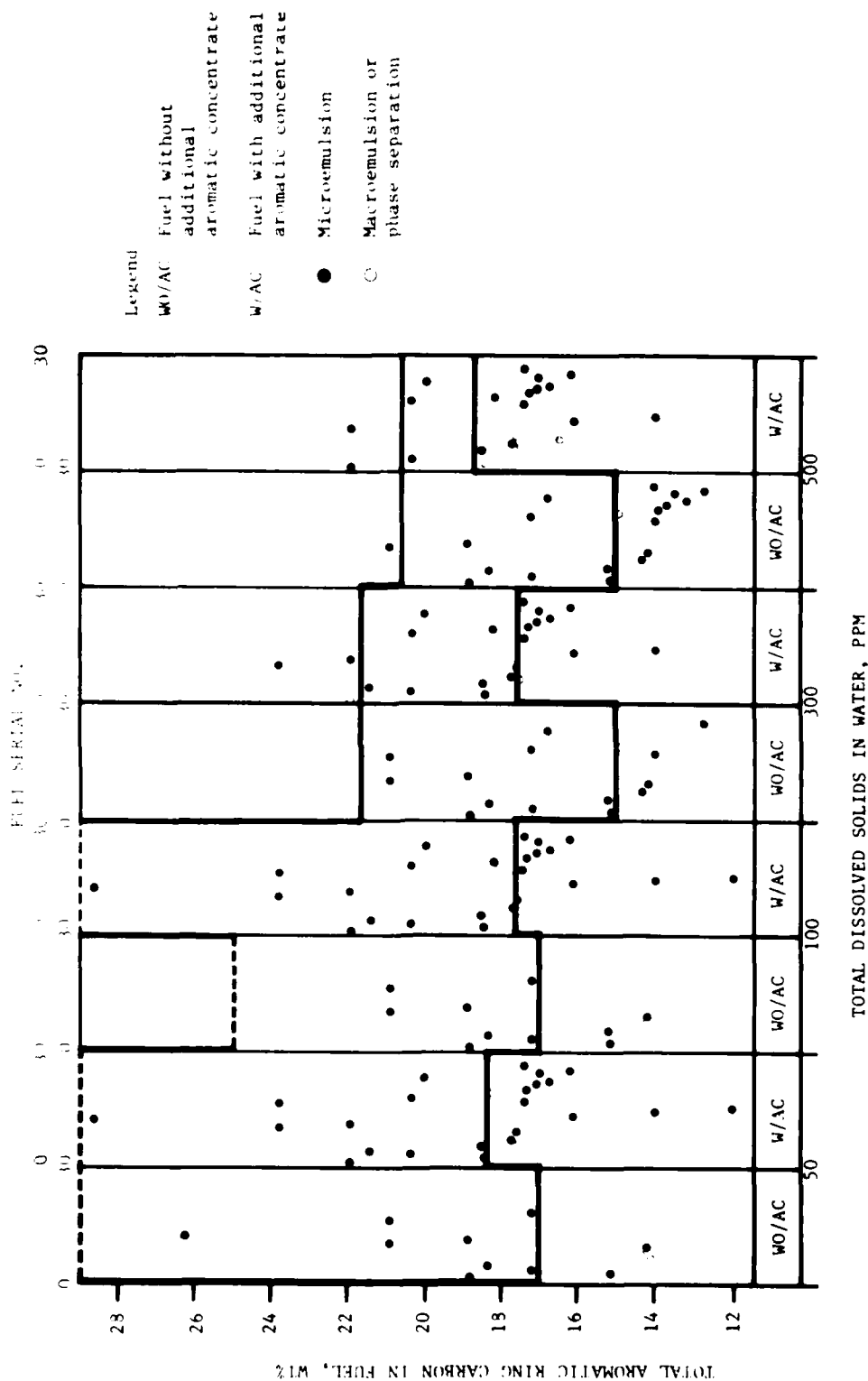


FIGURE 5b. INTERACTIONS BETWEEN FUEL TARC AND WATER TDS IN VARIOUS FUELS USING EA-97 (TAN - 17.1 mg KOH/g)

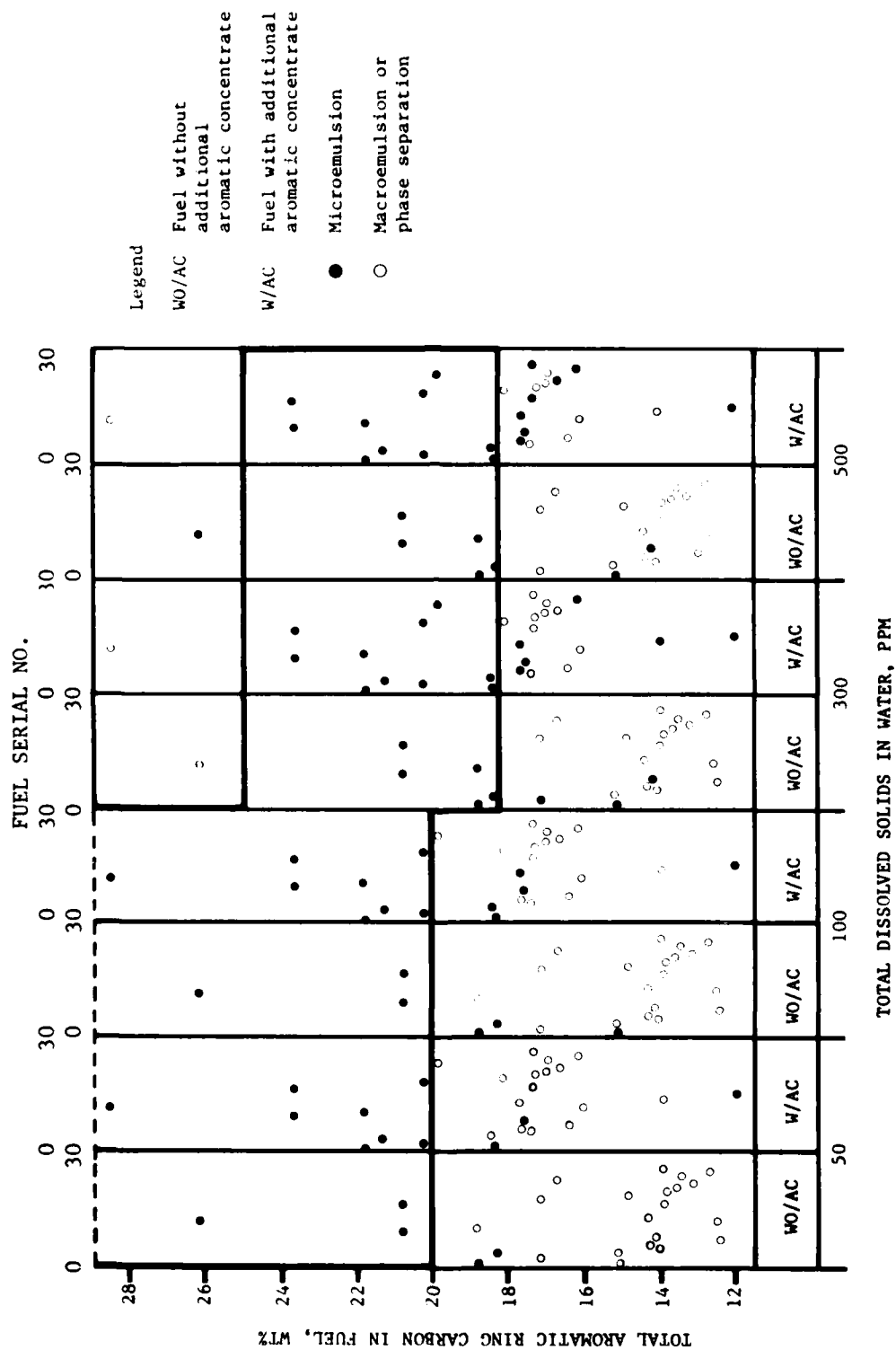


FIGURE 5c. INTERACTIONS BETWEEN FUEL TARC AND WATER TDS IN VARIOUS FUELS USING EA-90 (TAN = 19.0 mg KOH/g)

TABLE 5. ANALYSIS OF "BTX BOTTOMS" (CODE NO. 7481)

Density at 20°C, g/mL	0.8747
Flash Point, PMCC, °C	47
Refractive Index at 20°C	1.5006
Distillation, ASTM D 86,	Temp, °C
IBP	160
10%	162
50%	164
90%	170
95%	173
EP	190

Distillation by Gas Chromatography			
wt% off	at Temp, °C	wt% off	at Temp, °C
0.1	142	50	176
0.5	144	60	182
1	145	70	185
5	159	80	189
10	165	90	193
20	168	95	196
30	170	99	200
40	173	EP	334

Analysis of Aromatics by Gas Chromatography		Corrected
Retention Time, Minutes	Name*	vol%
25.59	ethylbenzene	0.07
25.90	(m + p) - xylene	0.56
26.54	o-xylene	1.79
27.17	i-propylbenzene	2.11
28.73	methylethylbenzene	32.78
28.75		10.29
28.86		6.36
29.28	1,2,4-trimethylbenzene	7.61
29.61	C ₉ + aromatics	0.61
30.07		13.15
30.30		11.40
30.51		6.00
31.29		6.67
31.76		0.27
32.17		0.28
32.56		0.02
24.12		0.02

Hydrocarbon Type Anal. by HPLC, aromatics, wt%	100
Hydrocarbon Type Anal. by FIA, aromatics, vol%	100
Aromatic Ring Carbon by UV, wt%	
Mononuclear	60.36
Dinuclear	1.36
Trinuclear	0.05
Total (TARC)	61.77

Nuclear Magnetic Resonance (NMR)

(a)	¹ H-NMR**	
	Aliphatic Protons, %	69.6
	Aromatic Protons, %	30.4
(b)	¹³ C-NMR***	
	Aliphatic Carbons, %	33.3
	Aromatic Carbons, %	67.7

* According to retention time only.

** Reference 9

*** Reference 8

TABLE 6. ANALYSIS OF COMMERCIAL AROMATIC CONCENTRATES

Code No.	7486	8908	10716	17047	10748	10749	10787	10788	10789	10790
Density at 20°C, g/mL	0.8747	0.8709	0.8646	0.8931	0.8854	0.8747	0.8758	0.8758	0.9315	0.9628
Flash Point, PMCC, °C	47	43	39	43	67	43	54	58	74	81
K Vis at 20°C, cSt	---	---	1.26	1.20	2.01	1.90	1.50	1.65	3.40	3.75
Refr. Index at 20°C	1.5006	---	1.4980	1.4986	1.5170	1.5105	1.5027	1.5045	1.5429	1.5725
FIA - saturates	0.0	---	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
olefins	Trace	---	0.6	0.4	0.4	0.5	0.4	0.4	0.4	0.4
aromatics	100	---	99.4	99.6	99.6	99.5	99.6	99.6	99.6	99.6
Arom. Ring Carbon, wt% (UV)										
mononuclear	60.36	58.58	52.81	53.43	49.60	52.22	55.28	54.33	39.44	21.44
dinuclear	1.36	3.12	1.65	2.37	6.50	4.98	2.46	4.24	18.33	49.63
trinuclear	0.05	0.00	0.00	0.00	0.15	0.05	0.00	0.03	1.39	0.49
total (TARC)	61.77	61.70	54.45	55.80	56.24	57.25	57.73	58.60	59.65	71.56
Distillation, ASTM D 86, °C										
IBP	160	---	157	154	184	170	164	177	195	201
5% evaporated	161	---	160	156	187	179	174	182	199	210
10% evaporated	162	---	161	157	188	181	174	183	204	214
50% evaporated	164	---	162	160	191	188	176	184	220	229
90% evaporated	170	---	169	165	200	202	178	189	238	239
95% evaporated	173	---	172	167	204	208	179	194	240	244
EP	199	---	194	194	231	234	204	221	254	261
Composition stated by supplier										
C ₈ + aromatics	---	---	---	---	---	97.5	99.8	99	---	---
C ₈ to C ₁₂ aromatics	---	---	---	98	98	---	---	---	---	---
Naphthalenes	---	---	---	---	---	---	---	8	---	99

TABLE 7. EFFECTS OF AROMATIC CONCENTRATE
ON FLASH POINT AND ON CETANE NUMBER

Base Fuel		Vol%			Flash Point, PMCC, °C**	Cetane No.
No.	Vol%	BTX*	EA-37	Water		
7225	100	--	--	--	61	48
7225	84	--	6	10	NF or 65	41
7225	78	6	6	10	61	39
7907	100	--	--	--	63	47
7907	78	6	6	10	NF	39
7909	100	--	--	--	54	47
7909	78	6	6	10	58	38
7931	100	--	--	--	88	47
7931	84	--	--	--	NF	40
7931	78	6	6	10	NF	38
7996	100	--	--	--	68	49
7996	78	6	6	10	NF	38
8445	100	--	--	--	75	40
8445	84	--	6	10	NF	33
8445	78	6	6	10	NF	31
8821	100	--	--	--	72	54
8821	78	6	6	10	NF	43
10200	100	--	--	--	--	56
10200	78	6	6	10	--	44

* BTX Code No. 7481

** NF = No flash point below 100°C

TABLE 8. FUEL COMPOSITION WINDOWS FOR NO-FAILURE, STABLE FRF
MICROEMULSION FORMATION WITH VARIOUS SURFACTANT
AND WATER COMPOSITIONS

Surfactant		Water		Aromatic Concentrate vol%	TARC, wt%		Total Aromatics, wt%	
vol%	TAN, mg KOH/g	vol%	TDS, ppm		Min	Max	Min	Max
6	15.5	10	50	0	15	26	25	40
6	15.5	10	50	6	12	22	--	--
6	15.5	10	100	0	15	19	28	32
6	15.5	10	100	6	12	19	--	--
6	15.5	19	300	0	15	17	--	--
6	15.5	10	300	6	14	17	--	--
6	17.1	10	50	0	17	28	31	50
6	17.1	10	50	6	18	28	--	--
6	17.1	10	100	0	17	26	31	42
6	17.1	10	100	6	18	28	--	--
6	17.1	10	300	0	17	26	34	40
6	17.1	10	300	6	18	22	--	--
6	17.1	10	500	0	15	21	--	--
6	17.1	10	500	6	19	22	--	--
6	19.0	10	50	0	19	28	34	50
6	19.0	10	50	6	20	28	--	--
6	19.0	10	100	0	19	28	34	50
6	19.0	10	100	6	20	28	--	--
6	19.0	10	300	0	17	26	34	42
6	19.0	10	300	6	18	28	--	--
6	19.0	10	500	0	18	26	34	42
6	19.0	10	500	6	18	28	--	--

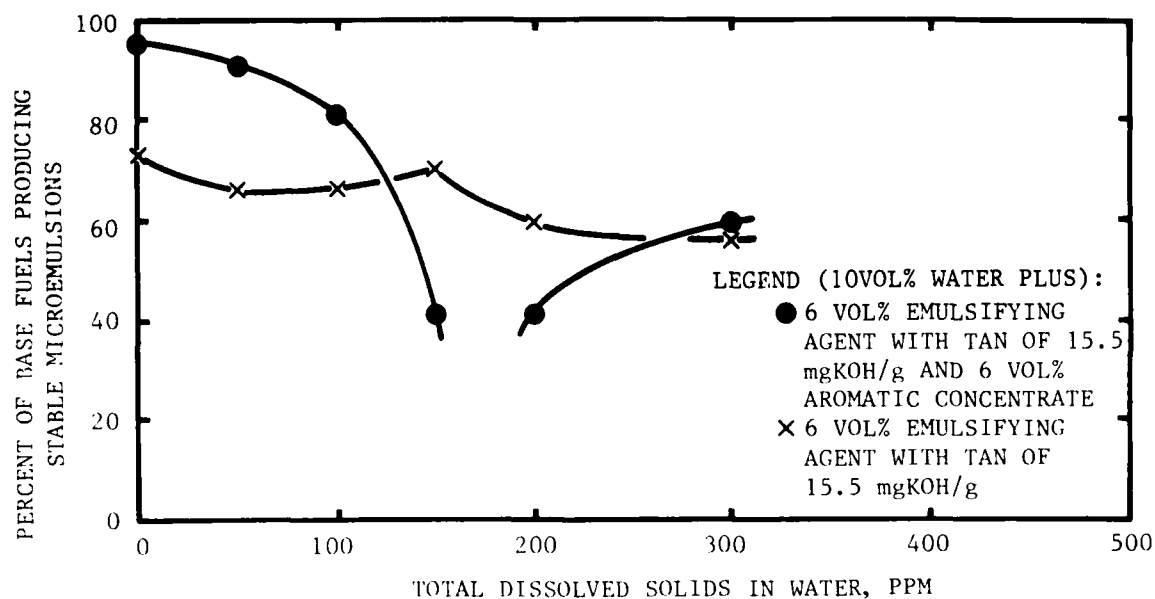


FIGURE 6a. EFFECT OF WATER COMPOSITION ON MICROEMULSION FORMATION--LOW TAN SURFACTANT

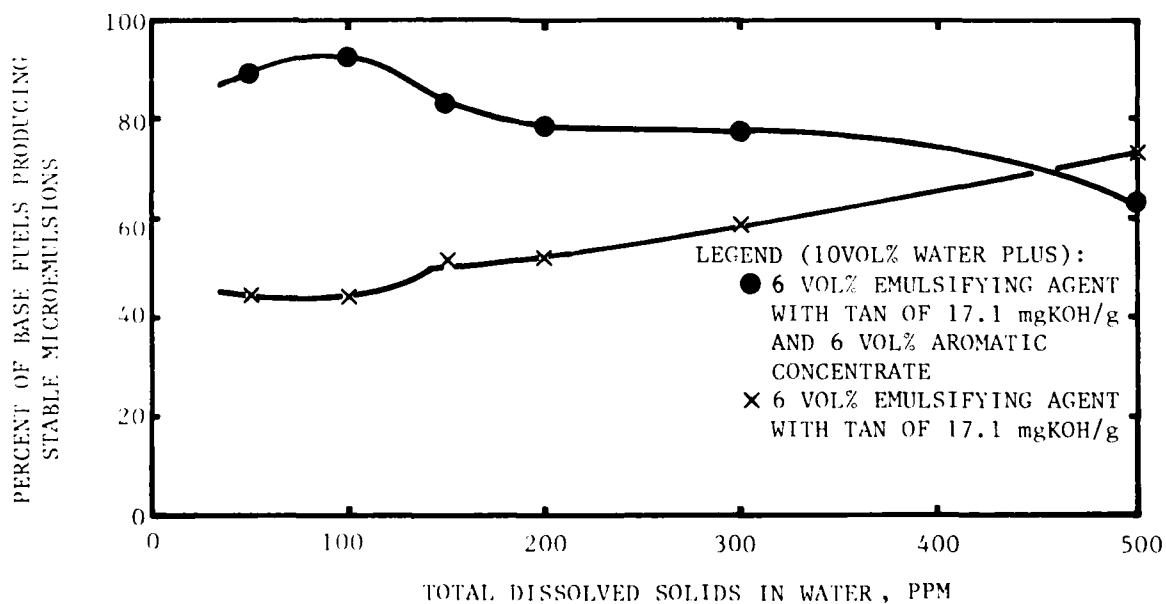


FIGURE 6b. EFFECT OF WATER COMPOSITION ON MICROEMULSION FORMATION--INTERMEDIATE TAN SURFACTANT

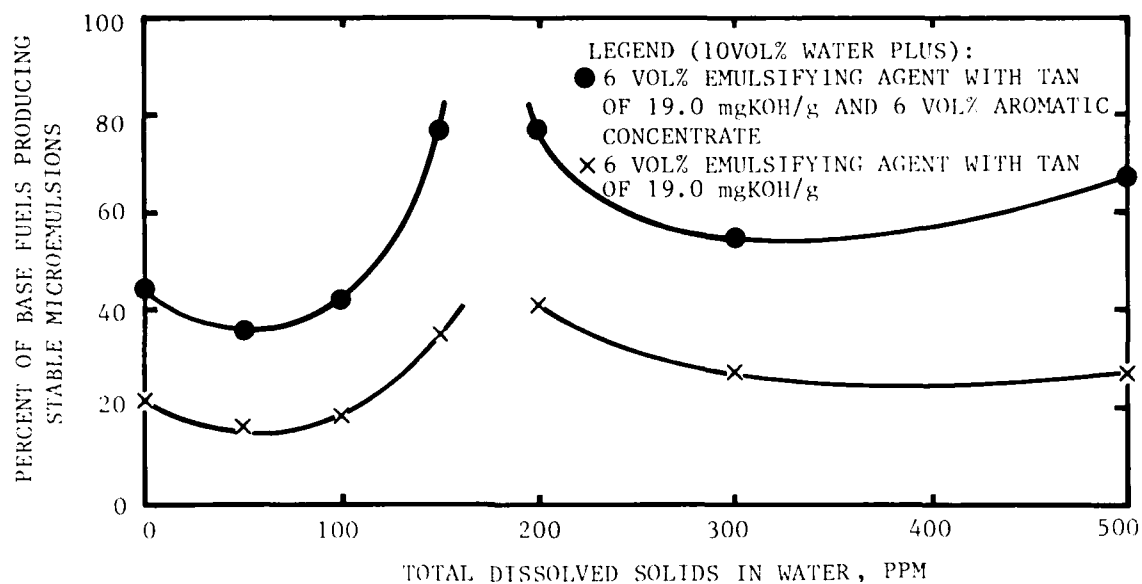


FIGURE 6c. EFFECT OF WATER COMPOSITION ON MICROEMULSION FORMATION--HIGH TAN SURFACTANT

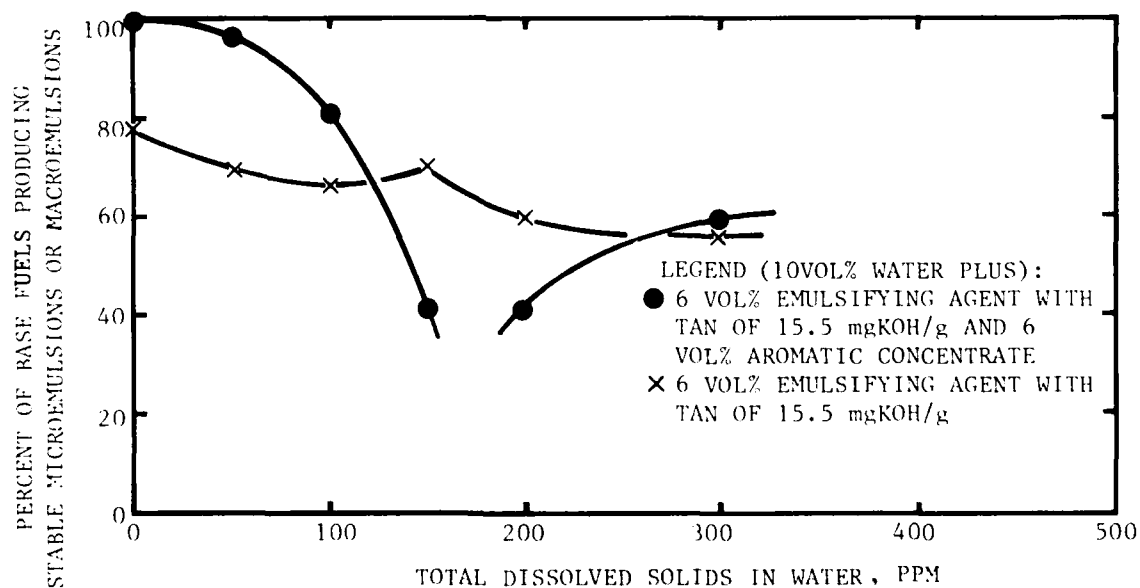


FIGURE 7a. EFFECT OF WATER COMPOSITION ON MICROEMULSION OR MACROEMULSION FORMATION--LOW TAN SURFACTANT

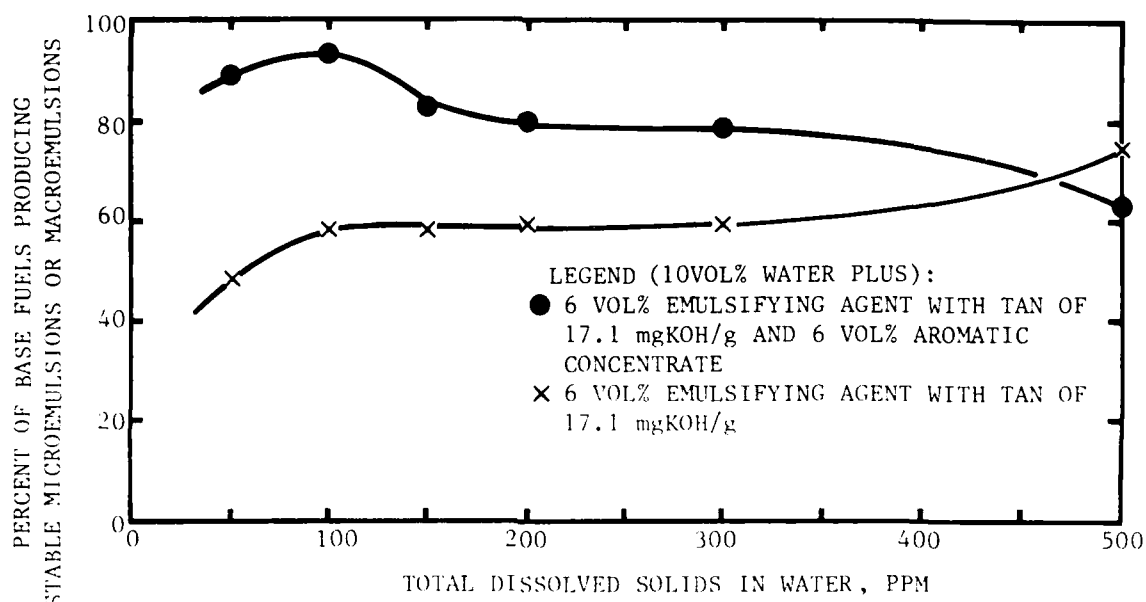


FIGURE 7b. EFFECT OF WATER COMPOSITION ON MICROEMULSION OR MACROEMULSION FORMATION--INTERMEDIATE TAN SURFACTANT

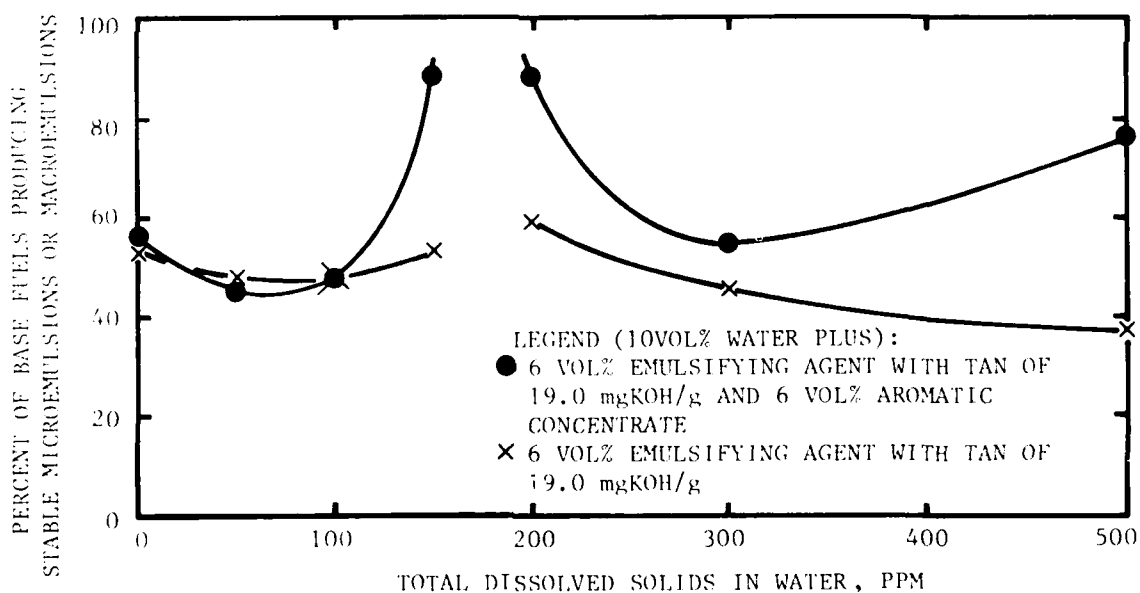


FIGURE 7c. EFFECT OF WATER COMPOSITION ON MICROEMULSION OR MACROEMULSION FORMATION--HIGH TAN SURFACTANT

TABLE 9a. EFFECT OF TDS ON FRF PHASE STABILITY
(TAN_{EA} = 15.5 mg KOH/g)

Arom. Conc. Added, Vol%	Rating*	Total Dissolved Solids in Water, ppm TDS											
		0			50			100			150		
		No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels
6	1	20	87.0	26	81.3	22	68.8	6	35.3	6	35.3	17	53.1
6	1T	0	0	0	0	1	3.1	0	0	1	5.9	2	6.3
6	2	0	0	1	3.1	0	0	0	0	0	0	0	0
6	2T	2	8.7	2	6.3	3	9.4	1	5.9	0	0	0	0
6	3	0	0	0	0	0	0	0	0	0	0	0	0
6	3T	1**	4.4	2**	6.3	0	0	0	0	0	0	0	0
6	4	0	0	0	0	0	0	0	0	0	0	0	0
6	5	0	0	1	3.1	6	18.7	9	52.9	5	29.4	4	12.5
6	6	0	0	0	0	0	0	1	5.9	5	29.4	9	28.1
0	1	15	68.2	18	56.3	19	59.6	9	52.9	7	41.2	17	53.1
0	1T	0	0	0	0	0	0	2	11.8	3	17.7	1	3.1
0	2	1	4.6	2	6.3	1	3.1	0	0	0	0	0	0
0	2T	0	0	1	3.1	1	3.1	1	5.9	0	0	0	0
0	3	0	0	0	0	0	0	0	0	0	0	0	0
0	3T	1**	4.6	1**	3.1	0	0	0	0	0	0	0	0
0	4	0	0	0	0	0	0	0	0	0	0	0	0
0	5	0	0	0	0	5	15.6	3	17.7	3	17.7	7	21.9
0	6	5	22.7	10	31.2	6	18.8	2	11.8	4	23.5	7	21.9
Total		23/22			32			32			17		
No. of Fuels		32			32			32			17		

* See footnote to Table 10 for definitions of ratings.
**Includes special, nonspecification fuel no. 8445.

TABLE 9b. EFFECT OF TDS ON FRF PHASE STABILITY
(TAN_{EA} = 17.1 mg KOH/g)

Arom. Conc. Added, Vol%	Rating*	Total Dissolved Solids in Water, ppm TDS											
		0			50			100			150		
		No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels
6	1	---	---	22	81.5	20	74.1	20	69.0	21	72.4	15	55.6
6	1T	---	---	1	3.7	4	14.8	3	10.3	2	6.9	6	22.2
6	2	---	---	0	0	0	0	0	0	0	0	0	0
6	2T	---	---	1	3.7	1	3.7	1	3.4	0	0	0	0
6	3	---	---	0	0	0	0	0	0	0	0	0	0
6	3T	---	---	0	0	0	0	0	0	0	0	0	0
6	4	---	---	0	0	0	0	0	0	0	0	0	0
6	5	---	---	0	0	0	0	2	6.9	3	10.3	2	7.4
6	6	---	---	3	11.1	2	7.4	3	10.3	3	10.3	4	14.8
0	1	---	---	11	40.7	12	44.4	13	44.8	14	48.3	12	44.4
0	1T	---	---	0	0	0	0	2	6.9	1	3.4	4	14.8
0	2	---	---	0	0	2	0	0	0	0	0	0	0
0	2T	---	---	1	3.7	0	0	0	0	0	0	0	0
0	3	---	---	0	0	0	0	0	0	0	0	0	0
0	3T	---	---	0	0	0	0	0	0	0	0	0	0
0	4	---	---	1	3.7	1	3.7	2	6.9	2	6.9	0	0
0	5	---	---	0	0	3	11.1	1	3.4	1	3.4	2	7.4
0	6	---	---	14	51.9	11	40.7	11	37.9	11	37.9	9	33.3
Total No. of Fuels		27	27	27	29	29	29	29	29	29	27	27	27

* See footnote to Table 10 for definitions of ratings.

TABLE 9c. EFFECT OF TDS ON FRF PHASE STABILITY
(TAN_{EA} = 19.0 mg KOH/g)

Arom. Conc. Added, Vol%	Rating*	Total Dissolved Solids in Water, ppm TDS											
		0			50			100			150		
		No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels	No. of Fuels	% of Fuels	No. of Fuels
6	1	10	40.0	12	36.4	14	42.4	13	76.5	13	76.5	16	48.5
6	1T	0	0	0	0	0	0	0	0	0	0	2	6.1
6	2	0	0	0	0	0	0	0	0	0	0	0	0
6	2T	1	4.0	0	0	0	0	0	0	0	0	0	0
6	3	0	0	0	0	0	0	0	0	0	0	0	0
6	3T	0	0	0	0	0	0	0	0	0	0	0	0
6	4	3	12.0	3	9.1	2	6.1	2	11.8	2	11.8	0	0
6	5	0	0	1	3.0	1	3.0	0	0	0	0	1	3.0
6	6	11	44.0	17	51.5	16	48.5	2	11.8	2	11.8	14	42.4
0	1	5	20.8	4	12.1	4	12.1	5	29.4	5	29.4	7	21.2
0	1T	0	0	0	0	1	3.0	0	0	0	0	2	6.1
0	2	0	0	1	3.0	1	3.0	1	5.9	2	11.8	0	0
0	2T	0	0	0	0	0	0	1	5.9	1	5.9	0	0
0	3	0	0	0	0	0	0	0	0	0	0	0	0
0	3T	0	0	0	0	0	0	0	0	0	0	0	0
0	4	8	33.3	11	33.3	10	30.3	3	17.6	3	17.6	6	18.2
0	5	0	0	0	0	1	3.0	0	0	0	0	1	3.0
0	6	11	45.8	17	51.5	16	48.5	7	41.2	6	35.3	17	51.5
Total		25/24			33			17			33		
No. of Fuels		33			33			17			33		

* See footnote to Table 10 for definitions of ratings.

Preparation of FRF at Various Temperatures:

Two No. 2 diesel fuels and a DFA were microemulsified with 10 vol% of water with the aid of 6 vol% of surfactant, nominally at 0°, 20°, 40°, and 50°C. In these experiments, the major portion of the base fuel was maintained within $\pm 0.5^\circ\text{C}$ of the desired temperature, and a surfactant-base fuel mixture (1:1 by volume) was then mixed into it. Finally, the water was added. Microemulsification was accomplished by a propeller-type mechanical stirrer. In each case, translucent product was obtained after the blend was allowed to return to room temperature without further mixing. At 0°C, all the emulsions appeared to be white macroemulsions. These experiments were repeated using 6 vol% of an aromatic concentrate (No. 10716, "BTX-bottoms") instead of an equal volume of base fuel. Identically good results were obtained. It may be concluded, therefore, that within the experimental limits, microemulsions could be made successfully at any temperature between 0° and 50°C.

Evaluation of Fire-Resistant Diesel Fuel

Visual Appearance:

To achieve maximum FRF stability, preparation of microemulsions was desirable. By definition, microemulsions are translucent systems. Visual observation of blends of FRF components through the circular bottles (25 mm in diameter, 150 mm high), in which a large number of compositions were made, was a quick and easy task. An FRF was acceptable if through this 25-mm path length the product was translucent with no more than a trace of cream. Such blends are pictured in Figures 8 and 9 with numbers of 5 or higher on the labels. In each of these figures, the pictures represent compositions in which 10 vol% water was dispersed in diesel fuels with one to ten vol% of surfactant, as shown on the labels. In Figure 8, the base fuel (No. 8821) conforms to VV-F-800B specifications, while the base fuel of Figure 9 meets the MIL-F-46162A(MR), Grade II specifications. At the extreme right of each of these pictures the unaltered base fuel is shown for reference.

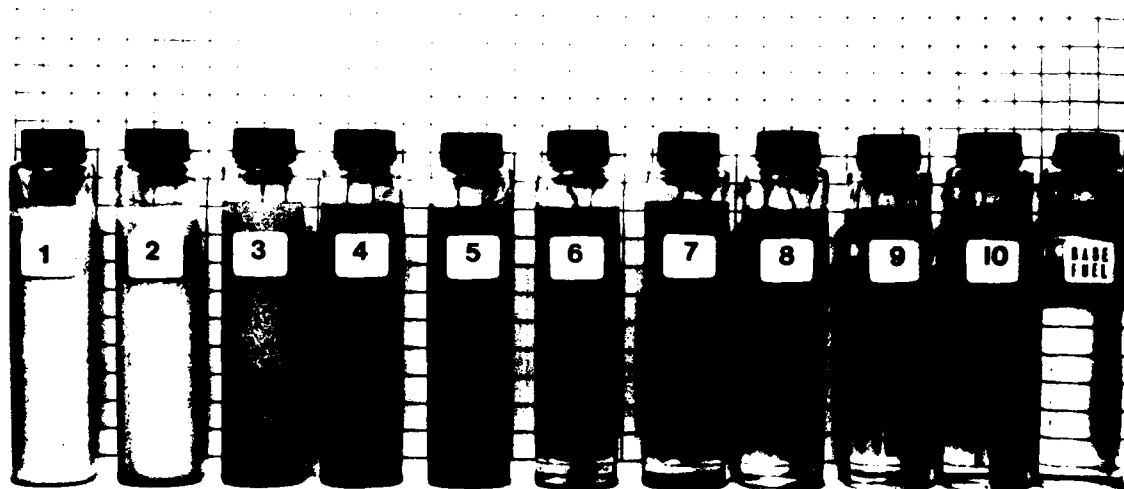


FIGURE 8. PHOTOGRAPH OF TEN BLENDS CONTAINING 84 VOLUME PARTS DIESEL FUEL (CODE NO. 8821), 10 VOLUME PARTS WATER (55 ppm TDS), AND THE VOLUME PARTS EMULSIFIER (TAN=15.5 mg KOH/g) INDICATED BY THE NUMBER OF EACH SAMPLE

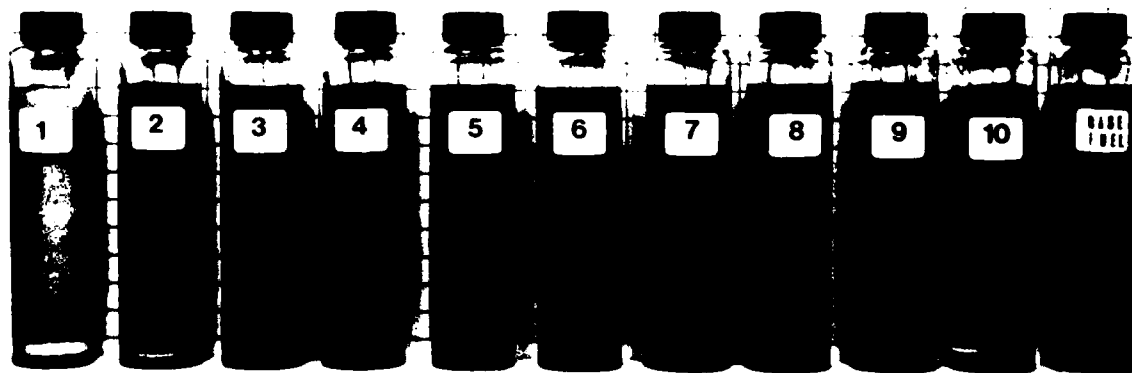


FIGURE 9. PHOTOGRAPH OF TEN BLENDS CONTAINING 84 VOLUME PARTS DIESEL FUEL (CODE NO. 7225), 10 VOLUME PARTS WATER (50 ppm TDS), AND THE VOLUME PARTS EMULSIFIER (TAN=15.5 mg KOH/g) INDICATED BY THE NUMBER ON EACH SAMPLE

This photograph shows the effects of changing water-to-surfactant ratios. As the volume ratio of water-to-surfactant is decreased from 10 to 1, the expected transition takes place from separate phases to visually homogeneous, transparent microemulsions.

Droplet Size Distribution:

Droplet size measurements were made on several aqueous diesel fuel microemulsions using photon correlation spectroscopy (PCS).(10) Measurements were made on a series of compositions (some of which are pictured in Figure 8) in which 10 vol% water had been dispersed with 5, 6, 8, and 10 vol% of surfactant in base fuel No. 8821. Each of these samples exhibited strong Rayleigh scattering. Assuming that the droplets within each of these emulsions are rigid monodisperse spheres, their solvated or hydrodynamic diameters were calculated. Evidence was found, however, that these emulsions were polydisperse with a geometric standard deviation of 1.64. These calculated diameters and the weight average diameters calculated assuming log-normal (L-N) or Rosin-Rammler (R-R) distribution functions are listed as follows:

vol% EA-98	D, Å	Weight Average Diameters, Å	
		"L-N"	"R-R"
5	385 ± 7	201 ± 8	177 ± 8
6	356 ± 8	191 ± 8	167 ± 7
8	310 ± 8	156 ± 7	137 ± 7
10	241 ± 7	115 ± 6	101 ± 6

The data are portrayed as log-normal distributions in Figure 10. State-of-art does not permit the selection of any of these data as absolute. It may be noted, however, that there is a trend toward smaller droplet size, and narrower droplet size distribution, as the water-to-surfactant ratio is lowered. Furthermore, these data may be considered only as a start in the detailed understanding of these microemulsions. Effects of the base fuel composition, water and surfactant quality, and water-to-surfactant ratio; temperature dependence; and influences of other parameters on the resultant emulsion droplet size distribution require additional research.

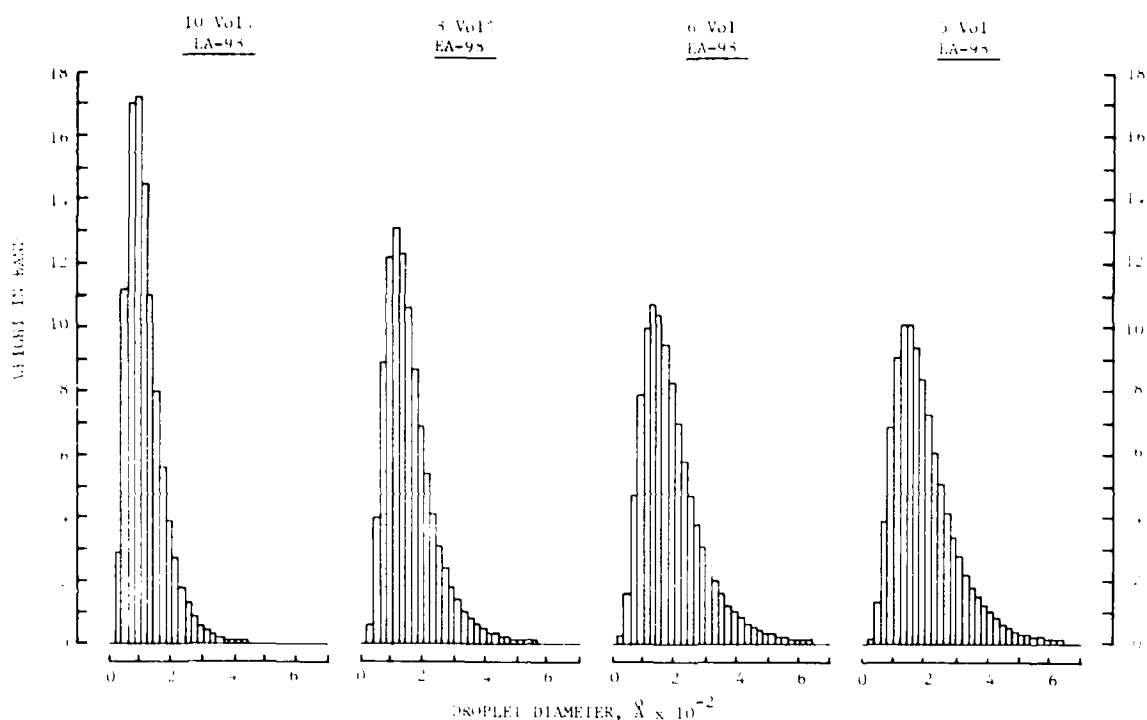


FIGURE 10. LOG-NORMAL DROPLET SIZE DISTRIBUTION OF FRF WITH VARIOUS SURFACTANT CONCENTRATIONS

Phase Stability:

Six-month storage tests were conducted with FRF compositions, prepared from two diesel fuels (Nos. 7225 and 8821) with deionized and tap water (10 vol%) and surfactant (6 vol%), and the results are summarized in Table 10. The total dissolved solids content of the tap water was approximately 300 ppm. The samples were stored under sheltered ambient conditions (October 1980 through April 1981, San Antonio, Texas), and at constant temperatures of 4°, 24°, and 40°C. In control experiments, the neat base fuels were also observed under identical conditions. Status of each of the samples was noted and photographed after each month of storage. None of the experimental conditions affected the base fuel meeting the VV-F-800B specifications (No. 8821), but a referee grade base fuel (No. 7225) meeting the MIL-F-46162A (MR), Grade II specifications, developed a black precipitate during the first month of storage under all test conditions. Adverse reactions were found during storage at 40°C, where FRFs survived for one month only. Under

all other tested conditions, all fuel blends survived the full test period without phase separation, except fuel No. 7225-based FRF that contained deionized water, which survived for over four months at 24°C storage conditions.

Temperature cycling experiments were performed on several FRFs having the following compositions:

Composition Code	Base Fuel		EA		TDS, ppm, in 10% Vol% Water
	No.	Vol%	No.	Vol%	
A	7225	84	96	6	50
B	7225	84	96	6	300
C	8821	84	99	6	50
D	8821	84	99	6	300
E	10200	84	99	6	50
F	10200	84	99	6	300

On each composition, six temperature cyclings were performed. Each cycle had the following schedule:

22 hours at 50°±2°C

4 hours at room temperature of approximately 27°C

22 hours at 2°±2°C

4 hours at room temperature of approximately 27°C

TABLE 10. SIX-MONTH STORAGE STABILITY OF FRF BLENDS

Months of Storage	Temp., °C	Ratings of Base Fuels ^a		Ratings of FRF Blends ^a			
		No. 7225	No. 8821	No. 7225/DI ^b	No. 7225/Tap ^c	No. 8821/DI ^d	No. 8821/Tap ^e
0	4	1	1	1	1	1	1
1	4	1 + black ppt	1	1	1	1	1
2	4	1 + black ppt	1	3	1T	1	1
3	4	1 + black ppt	1	3T	1T	1	1
4	4	1 + black ppt	1	2	1	1	1
5	4	1 + black ppt	1	2	1	1	1
6	4	1 + black ppt	1	2	1	1	1
0	24	1	1	1	1	1	1
1	24	1 + black ppt	1	1	1	1	1
2	24	1 + black ppt	1	1	1	1	1
3	24	1 + black ppt	1	1	1	1	1
4	24	1 + black ppt	1	2	2	1	1
5	24	1 + black ppt	1	6	2	2	1
6	24	1 + black ppt	1	6	2	2	2
0	40	1	1	1	1	1	1
1	40	1 + black ppt	1	1	1	1	1
2	40	1 + black ppt	1	6	3	6	6
3	40	1 + black ppt	1	6	3	6	6
4	40	1 + black ppt	1	3	3	6	6
5	40	1 + black ppt	1	4	4	6	6
6	40	1 + black ppt	1	4	4	6	6
0	f	1	1	1	1	1	1
1	f	1 + black ppt	1	1	1	1	1
2	f	1 + black ppt	1	1	1	1	1
3	f	1 + black ppt	1	1	1T	1T	1T
4	f	1 + black ppt	1	1	1	1	1
5	f	1 + black ppt	1	1	1	1	1
6	f	1 + black ppt	1	2	1	1	1

(a) Ratings of hand-shaken samples:

- 1 - transparent
- 2 - translucent microemulsion
- 3 - Whitish-brown macroemulsion
- 4 - Whitish-yellow macroemulsion
- T - Emulsion with trace cream (≤ 0.5 vol%)
- 5 - Emulsion that contains cream (≤ 2 vol%)
- 6 - Phase separation

(b) 10 vol% deionized water stabilized by 6 vol% EA-79, TAN = 19.0 mg KOH/g.

(c) 10 vol% tap water stabilized by 6 vol% EA-79

(d) 10 vol% deionized water stabilized by 6 vol% EA-78, TAN = 19.0 mg KOH/g.

(e) 10 vol% tap water stabilized by 6 vol% EA-78.

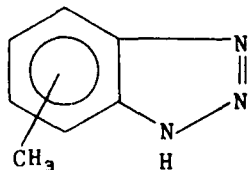
(f) Sheltered ambient.

After each step of each cycle, the samples were visually rated before and after shaking them. The experimental results are summarized in Table 11. It was observed that during the cold-temperature cycles, most samples exhibited phase separation; however, they spontaneously rehomogenized during their stay at room temperature. High-temperature periods had no ill effects on any of the samples. It may be concluded, therefore, that all the samples successfully survived these temperature cycling experiments.

Corrosion Characteristics:

As reported earlier (1), the surfactant used in FRF blends functions as an efficient corrosion inhibitor for steel. This has been further documented by comparing results obtained with the NACE (TM-01-72) pipeline corrosion test for three base fuels (Code Nos. 7225, 8821, and 11016) and FRF blends made from them with 6 vol% surfactant, EA-99, 6 vol% AC, and 10 vol% water with 50 ppm TDS. The ratings for the base fuels were A, B++ (essentially the same as A), and C (rusty), respectively. The ratings for the corresponding FRF blends were A, B++, and A, respectively. These results confirm the general applicability of the previously reported results for steel specimens.

Corrosion of copper and its alloys may take place in the presence of FRF, due to the amine content of the surfactant. (Some commercial diesel fuels contain inhibitors that alleviate this type of corrosion. This corrosion could be effectively eliminated by the presence of tolyltriazole:



at a concentration of approximately 500 ppm in the FRF. This product is soluble in aliphatic alcohols, amines, and ketones, but only marginally soluble in mineral oils and fuels. For this reason, it was predissolved in the surfactant at about 50°C prior to the blending operation.

TABLE 11. PHASE STABILITY DURING TEMPERATURE CYCLING OF FRF

Cycle No.	Exposure °C	Hr	A			B			C			D			E			F		
			As	Is	Mixed	As	Is	Mixed	As	Is	Mixed	As	Is	Mixed	As	Is	Mixed	As	Is	Mixed
1	2	22	IT		1	IT		1	6		1	6		1	6		6	6		6
	27	4	1		1	1		1	1		1	1		1	1		1	1		1
	51	22	1		1	1		1	1		1	1		1	1		1	1		1
	27	4	IT		1	IT		1	IT		1	IT		1	IT		IT	IT		IT
2	2	22	IT		1	IT		1	6		1	6		1	6		6	6		6
	27	4	1		1	1		1	1		1	1		1	1		1	1		1
	51	22	1		1	1		1	1		1	1		1	1		1	1		1
	27	70	IT		1	IT		1	IT		1	IT		1	IT		IT	IT		IT
3	2	22	IT		1	IT		1	6		1	6		1	6		6	6		6
	27	4	1		1	1		1	1		1	1		1	1		1	1		1
	51	22	1		1	1		1	1		1	1		1	1		1	1		1
	27	4	IT		1	IT		1	IT		1	IT		1	IT		IT	IT		IT
4	2	22	IT		1	IT		1	6		1	6		1	6		6	6		6
	27	4	1		1	1		1	1		1	1		1	1		1	1		1
	51	22	1		IT	1		IT	1		IT	1		IT	1		IT	IT		IT
	27	4	IT		1	IT		1	IT		1	IT		1	IT		IT	IT		IT
5	2	22	IT		1	IT		1	6		1	6		1	6		6	6		6
	27	4	1		1	1		1	1		1	1		1	1		1	1		1
	51	22	1		IT	1		IT	1		IT	1		IT	1		IT	IT		IT
	27	4	IT		1	IT		1	IT		1	IT		1	IT		IT	IT		IT
6	2	22	IT		1	IT		1	6		1	6		1	6		6	6		6
	27	4	1		1	1		1	1		1	1		1	1		1	1		1
	51	22	1		IT	1		IT	1		IT	1		IT	1		IT	IT		IT
	27	4	IT		1	IT		1	IT		1	IT		1	IT		IT	IT		IT

Notes: Compositions A through F are defined in text.

"Mixed" (shaken) samples' ratings taken 60 min after "as is" (undisturbed) ratings.

Ratings: 1 = translucent microemulsion

T = sample contained a trace of cream.

6 = phase separation of over 2 vol%.

Corrosion tests were performed at 55°C for 100 and 200 hours in the presence of specimens:

- copper, electrolytic, alloy No. 110 (Cu, 99.9%)
- bronze, alloy No. 836 (Cu, 85%; Sn, Pb, Zn, 5% each)
- brass, "cartridge brass," alloy No. 260 (Cu, 70%; Zn, 30%)

These were partially immersed in the test fluids. Each specimen caused development of a greenish tint in the FRF, which was noticeable even in the presence of 1000 ppm of inhibitor. At the conclusion of the test, it was found that best protection was provided for copper, and least for brass. Essentially no vapor phase protection was provided in any of the cases. As expected, the exposure conditions were too severe for the FRF, as most samples suffered phase separation before the test was concluded.

Other Physical Properties:

Surface tension and DC electrical conductivity measurements were made on FRF early in the program. These measurements indicated no appreciable difference between the referee-grade base fuel (No. 7225) and FRF blends made from it.

Viscosity anomalies have been occasionally noted while preparing laboratory-scale FRF samples. "Normally" the FRF is about 50 to 60 percent more viscous than the base fuel from which it was made. It was observed, however, that FRF prepared from certain fuels--for as yet unknown proven reasons--appears much more viscous than expected. Kinematic viscosity measurements at 40°C did not give data that corresponded to the usual observations, but data at 20°C showed that the "normal" FRFs exhibited kinematic viscosity values between 6 and 15 cSt, the "viscous" FRFs about 30 cSt, while the "very viscous" FRFs had a viscosity of about 100 cSt. These viscosity values did not remain constant but decreased with time.

Because of these observations, a series of experiments was conducted to further explore the viscosity effects in a single FRF. The study was carried out at the temperatures of 25° and 40°C on a DF-2-based FRF (84 vol%

8821 + 6 vol% EA-99 + 10 vol% H₂O). The blend was prepared at 25°C. Immediately after preparation, the emulsion was continuously stored in individual capped single-bulb viscometer tubes at 25° and 40°C. The viscosity data in Columns 2 and 3 of Table 12 were collected on these two individual

TABLE 12. EFFECT OF AGING ON VISCOSITY OF FRF

Age of Emulsion Days after Prep.	Viscosity (Centistokes)		Four-Bulb Viscosity at 40°C (Centistokes)			
	25°C	40°C	Bulb 1	Bulb 2	Bulb 3	Bulb 4
(2 Hr)	44.9	5.7	5.5	5.5	5.5	5.8
1	22.2	5.7	5.3	5.9	5.4	5.4
4	16.8	5.7	5.3	5.3	5.3	5.3
5	14.1	5.6	5.3	5.3	5.3	5.3
6	13.1	5.5	5.3	5.3	5.3	5.4
7	11.1	5.5	5.3	5.3	5.4	5.2
8	10.4	5.5	5.3	5.3	5.3	5.3
11	9.9	5.5	5.2	5.2	5.2	5.2
12	9.7	5.5	5.3	5.2	5.3	5.3
13	9.5	5.5	5.2	5.3	5.3	5.2
14	9.5	5.5	5.3	5.3	5.2	5.4
18	9.3	5.4	5.2	5.2	5.2	5.2
19	9.2	5.4	5.2	5.2	5.2	5.2
20	9.2	5.3	5.4	5.2	5.2	5.2
21	9.2	5.3	5.1	5.1	5.2	5.5
22	9.2	5.2	5.2	5.2	5.2	5.2
25	9.1	5.2	5.1	5.2	5.2	5.2
26	9.1	5.2	5.3	5.2	5.2	5.2
27	9.0	5.1	5.2	5.2	5.2	5.2
28	9.0	5.1	5.2	5.2	5.2	5.2
29	9.0	5.1	5.2	5.2	5.2	5.2
30	9.0	5.0	5.2	5.2	5.2	5.2

samples over a 30-day period. These data show a trend in decreasing viscosity over the 30-day period. The four-bulb viscosimeter data at 40°C show no difference with various shear rates (bulbs) on a given day, thus exhibiting Newtonian characteristics at 40°C. The four-bulb viscometer data were collected with a fresh sample from a capped bottle stored continuously at 40°C for every measurement.

Following these viscosity studies, a series of blends of base fuels with and without FRF components was subjected to properties measurements, including additional viscosity determinations, and these results are presented in Tables 13a and 13b. Thereby comparisons can be made among samples prepared at the same time.

Kinematic viscosity was measured on several blends between 10° and 50°C at 10°C intervals. Between 20° and 50°C, no anomalous results were found. At 10°C, two FRFs showed higher than expected viscosities (17.2 and 32.1 cSt for Composition Nos. 9 and 15, respectively). Shear-dependent viscosity was noted only in the case of Composition No. 13 at 10°C. This same FRF also exhibited time-induced lowering of viscosity at 10°C, as shown in Table 13b.

Accelerated oxidation stability measurements, according to ASTM D 2274, were found to be inconclusive, as some trend reversals were observed. Compositions containing base fuels Nos. 7225 and 8821 show slightly increased values (lower stability ratings) when EA was mixed into the base fuels, and further increases in the results when both EA and AC were mixed with the base fuels. Substantially better ratings were found on the finished FRFs. In the case of base fuel No. 10200, which was obtained from a local major oil company service station, the lowest stability was observed in case of the base fuel, with successively higher stability (lower ASTM D 2274 values) as FRF ingredients were added to the fuel. In each of the tested cases, the FRF passed the 1.0 mg/100 ml test limit, even if the base fuel failed it.

TABLE 13a. SELECTED PROPERTIES OF FRFS AND THEIR COMPONENTS

Series No.	Composition, Volume Parts				Fuel Temp., °C	Flash Pt., °C	Cloud Point, °C	Pour Point, °C	Flash Pt., °C	Settling, %	Octane No.	Kinematic Viscosity, cSt, at °C			
	Base Fuel No.	1000	1000	1000								10	20	30	50
1	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
2	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
3	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
4	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
5	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
6	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
7	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
8	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
9	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
10	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
11	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
12	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
13	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
14	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
15	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
16	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
17	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
18	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
19	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
20	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
21	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
22	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
23	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100
24	8821	100	100	100	100	100	100	100	100	100	100	100	100	100	100

a = Methyl Isobutyl Fuel
 b = Methyl Isobutyl Fuel
 c = Methyl Isobutyl Fuel
 d = Methyl Isobutyl Fuel
 e = Methyl Isobutyl Fuel
 f = Methyl Isobutyl Fuel
 g = Methyl Isobutyl Fuel
 h = Methyl Isobutyl Fuel
 i = Methyl Isobutyl Fuel
 j = Methyl Isobutyl Fuel
 k = Methyl Isobutyl Fuel
 l = Methyl Isobutyl Fuel
 m = Methyl Isobutyl Fuel
 n = Methyl Isobutyl Fuel
 o = Methyl Isobutyl Fuel
 p = Methyl Isobutyl Fuel
 q = Methyl Isobutyl Fuel
 r = Methyl Isobutyl Fuel
 s = Methyl Isobutyl Fuel
 t = Methyl Isobutyl Fuel
 u = Methyl Isobutyl Fuel
 v = Methyl Isobutyl Fuel
 w = Methyl Isobutyl Fuel
 x = Methyl Isobutyl Fuel
 y = Methyl Isobutyl Fuel
 z = Methyl Isobutyl Fuel

TABLE 13b. FOUR-BULB VISCOSITY OF 10200-BASED FRF

Temp., °C	Kin. Viscosity, cSt, Bulb No.				Repeat Kin. Viscosity, cSt, Bulb No.			
	1	2	3	4	1	2	3	4
10	200.1	234.3	255.2	259.7	195.4	216.2	230.3	235.7
20	11.5	11.7	11.6	11.5	10.0	10.1	10.2	10.1
30	4.8	4.8	4.9	4.9	4.8	4.8	4.8	4.9
40	3.9	3.9	4.0	4.0	3.9	3.9	4.0	4.0
50	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3

Cetane numbers (CN) change with composition as illustrated in Table 13a. In each case, the base fuel showed the highest CN. Addition of 12 vol parts of equivolume mixture of EA and AC resulted in drop of CN by 3, 5, and 6 units for base fuels Nos. 7225, 8821, and 10200, respectively. An additional drop of six cetane numbers was observed when 10 vol parts of water was microemulsified in the base fuel-EA-AC mixture.

Cloud points were determined on each of the blends, except on the FRF compositions, because the latter were hazy under all conditions.

Pour points were also measured. No drastic changes were observed within any groups.

Flash point (PMCC Method) measurements indicated results similar to those observed and listed elsewhere in this report. Of four FRF compositions, three gave observable flash points, but one of the FRFs gave no flash point (the one containing base fuel with a flash point of 74°C).

In NACE corrosion tests, each of the examined FRFs earned an "A" rating (no rusting), even if the base fuel gave a "C" rating (25-50 percent of the surface rusted).

Fuel Dilution Effects

To determine fuel dilution effects, 12 vol% of a 50 vol% solution of EA-99 [Total Acid No. (TAN) = 15.5 mg KOH/g] in aromatic concentrate (AC) No. 10716 was used to microemulsify 10 vol% of water (containing 10 and 100 ppm of total dissolved solids, TDS, as calcium nitrate) in diesel fuel Nos. 7225 and 8821. Each of these four FRF blends was diluted with each of the base diesel fuels at 10-percent intervals. The experimental results are summarized in Table 14. Evaluation of the available data indicates that while some mildly adverse effects may arise, manifested as increased haziness, each of the compositions remained microemulsions. Normally, if an FRF was diluted with the base fuel from which it was made, the diluted product became clearer with increasing dilution. If the FRF was diluted with another

TABLE 14. DILUTION OF FRF WITH BASE FUELS

Serial No.	Volume Percent				Rating After	
	FRF No. 1	FRF No. 2	BF No. 1	BF No. 2	24 Hours	2 Weeks
1	100	0	0	0	1	1
2	90	0	10	0	1	1
3	80	0	20	0	1	1
4	70	0	30	0	1	1
6	50	0	50	0	1	1
7	40	0	60	0	1	1
8	30	0	70	0	1	1
9	20	0	80	0	1	1
10	10	0	90	0	1	1
11	90	0	0	10	1	1
12	80	0	0	20	1	1
13	70	0	0	30	1	1
14	60	0	0	40	2	1T
15	50	0	0	50	2	1T
16	40	0	0	60	2	1T
17	30	0	0	70	3	1T
18	20	0	0	80	1	1
19	10	0	0	90	1	1
20	0	100	0	0	1	1
21	0	90	10	0	1	1
22	0	80	20	0	1	1
23	0	70	30	0	1	1
24	0	60	40	0	1	1
25	0	50	50	0	1	1
26	0	40	60	0	1	1
27	0	30	70	0	1	1
28	0	20	80	0	1	1
29	0	10	90	0	1	1
30	0	90	0	10	1	1
31	0	80	0	20	1	1
32	0	70	0	30	1	1
33	0	60	0	40	1	1
34	0	50	0	50	3	1T
35	0	40	0	60	2	1T
36	0	30	0	70	2	1T
37	0	20	0	80	2	1T
38	0	10	0	90	1T	1T

FRF No. 1 comprises base fuel No. 8821 (84 vol%) + 1:1 (by vol.) mixture of
EA-99 and AC No. 10716 (12 vol%) + water, 10 ppm TDS in water (10 vol%)

FRF No. 2 as FRF No. 1 but with 100 ppm TDS in water

FRF No. 3 as FRF No. 1 but with base fuel No. 7225

FRF No. 4 as FRF No. 3 but with 100 ppm TDS in water

BF No. 1 base fuel No. 8821

BF No. 2 base fuel No. 7225

Emulsion Rating:

1. Transparent microemulsion
2. Translucent microemulsion
3. Whitish-brown macroemulsion
4. Whitish-yellow macroemulsion
5. Trace of cream (≤ 0.5 vol%)
6. Contains cream (≤ 2 vol%)
7. Phase separation

TABLE 14. DILUTION OF FRF WITH BASE FUELS-FRF
(CONT'D)

Serial No.	Volume Percent				Rating After	
	FRF No. 3	FRF No. 4	BF No. 1	BF No. 2	24 Hours	2 Weeks
1	100	0	0	0	1	1T
2	90	0	10	0	2T	1T
3	80	0	20	0	2T	1T
4	70	0	30	0	2T	1T
5	60	0	40	0	2T	1T
6	50	0	50	0	2T	1T
7	40	0	60	0	1T	1T
8	30	0	70	0	1	1
9	20	0	80	0	1	1
10	10	0	90	0	1	1
11	90	0	0	10	1T	1T
12	80	0	0	20	1T	1T
13	70	0	0	30	1T	1T
14	60	0	0	40	1T	1T
15	50	0	0	50	1T	1T
16	40	0	0	60	1T	1T
17	30	0	0	70	1T	1T
18	20	0	0	80	1T	1T
19	10	0	0	90	1T	1T
20	0	100	0	0	2T	1T
21	0	90	10	0	2T	1T
22	0	80	20	0	2T	1T
23	0	70	30	0	2T	1T
24	0	60	40	0	2T	1T
25	0	50	50	0	1T	1T
26	0	40	60	0	1	1
27	0	30	70	0	1	1
28	0	20	80	0	1	1
29	0	10	90	0	1	1
30	0	90	0	10	2T	1T
31	0	80	0	20	2T	1T
32	0	70	0	30	2T	1T
33	0	60	0	40	2T	1T
34	0	50	0	50	2T	1T
35	0	40	0	60	2T	1T
36	0	30	0	70	1T	1T
37	0	20	0	80	1T	1T
38	0	10	0	90	1T	1T

FRF No. 1 comprises base fuel No. 8821 (84 vol%) + 1:1 (by vol.) mixture of
EA-99 and AC No. 10716 (12 vol%) + water, 10 ppm TDS in water (10 vol%)

FRF No. 2 as FRF No. 1 but with 100 ppm TDS in water

FRF No. 3 as FRF No. 1 but with base fuel No. 7225

FRF No. 4 as FRF No. 3 but with 100 ppm TDS in water

BF No. 1 base fuel No. 8821

BF No. 2 base fuel No. 7225

Emulsion Rating:

1. Transparent microemulsion
2. Translucent microemulsion
3. Whitish-brown macroemulsion
4. Whitish-yellow macroemulsion
- T. Trace of cream (≤ 0.5 vol%)
5. Contains cream (≤ 2 vol%)
6. Phase separation

base fuel, slight increases in haziness were observed within an intermediate dilution range.

It should be noted, however, that base fuel No. 7225 is an atypical (referee grade) fuel with high volatility and high total aromatic ring carbon (TARC) content. The additional AC in the composition elevated the already high 18.9 wt% TARC content of the fuel component to 21.9 wt%. The corresponding TARC contents of base fuel No. 8821 are 14.4 and 17.8 wt%, respectively.

Effects of Diesel Fuel Additives:

A limited number of experiments has shown that none of the examined fuel oil additives had adverse effects on FRF phase stability. The studied additives included an alkyl-phenylenediamine antioxidant, and a multicomponent fuel oil additive package. The effects of cetane number improver on FRF preparation and phase stability were investigated. Cetane number (CN) improver 2-ethylhexyl nitrate was used at various concentrations in several FRF composition as summarized in Table 15. Two base diesel fuels were used in this study, both with "average" total aromatic ring carbon (TARC) concentrations. One of these fuels, No. 8821, was obtained from a refinery; the other, No. 10200, was purchased from a local service station. It is not known if either of these fuels contained any additives at the time of their procurement. Both fuels were microemulsified into FRF formulations "as received," and also modified by the addition of an aromatic concentrate (No. 10716) to increase their respective TARC contents. For each case, 10 vol% of San Antonio tap water, containing about 300 ppm of total dissolved solids, was microemulsified by the aid of 6 vol% of emulsifying agent EA-78 (TAN = 15.5 mg KOH/g). Since Federal Specification VV-F-800 allows the use of up to 0.5 vol% of CN-improving compound in diesel fuels, in the test matrix from 0 to 1 vol% of this compound was used. Cetane number improver was added at one of two stages of FRF preparation: (1) it was mixed with the base diesel fuel before the addition of any other FRF component, and (2) it was blended into the prefinished FRF composition. The results indicate that in the studied cases the CN improver was fully compatible with FRF blends, although in case (1), freshly made fuel No. 8821 based FRFs were hazier in the presence of 2-ethylhexyl nitrate than without it. This haze, however,

TABLE 15. EFFECT OF A CETANE NUMBER IMPROVER ON
FRF PREPARATION AND PHASE STABILITY

Sample No.	Base Fuel No.	Fuel Vol%	CN Imp,(1) Vol%	AC 10716,(2) Vol%	Fuel Comp. TARC, Wt%	EA-99,(3) Vol%	Water, Vol%	Visual (5)	Rating(4) (6)
2	8821	83.9	0.1	-	14.4	6	10	1T	1
3	8821	83.7	0.3	-	14.4	6	10	1T	1
4	8821	83.5	0.5	-	14.4	6	10	1T	1
5	8821	83.0	1.0	-	14.4	6	10	1T	1
6	8821	78.0	0.0	6	17.3	6	10	1T	1
7	8821	77.9	0.1	6	17.3	6	10	1T	1
8	8821	77.7	0.3	6	17.3	6	10	1T	1
9	8821	77.5	0.5	6	17.3	6	10	1T	1
10	8821	77.0	1.0	6	17.3	6	10	1T	1
11	10200	84.0	0.0	-	14.0	6		1	1
12	10200	83.9	0.	-	14.0	6	10	1	1
13	10200	83.7	0.3	-	14.0	6	10	1	1
14	10200	83.5	0.5	-	14.0	6	10	1	1
15	10200	83.0	1.0	-	14.0	6	10	1	1
16	10200	78.0	0.0	6	17.0	6	10	1	1
17	10200	77.9	0.1	6	17.0	6	10	1	1
18	10200	77.7	0.3	6	17.0	6	10	1	1
19	10200	77.5	0.5	6	17.0	6	10	1	1
20	10200	77.0	1.0	6	17.0	6	10	1	1

1 Cetane No. Improver DII-3 from Ethyl Corp.

2 Aromatic Concentrate

3 Total Acid No. = 15.5 KOH/g

4 Rating of "1" = translucent microemulsion
"T" = contains a trace of cream

5 CN improver mixed into base fuel before addition of
other FRF components

6 CN improver added to prefinished FRF

cleared up upon standing overnight. In the other compositions, the added CN improver showed no visible effects.

Effects of Carbon Dioxide:

Effects of carbon dioxide on the efficacy of the surfactant were investigated. About 400 g of surfactant were bubbled with dried, bottled CO_2 at a rate of 0.83 ml/min for 0, 1, 5, 15, 30, 60 and 120 minutes. The untreated surfactant sample provided good microemulsification in a variety of diesel fuels with deionized water. Phase separation took place in each case where CO_2 -treated surfactant was used. The CO_2 uptake undoubtedly stems from its reaction with the diethanolamine in the surfactant mixture. When preparation of FRF was attempted in fully open vessels, atmospheric CO_2 was drawn into the composition during mixing of the ingredients with a simple stirrer, and this resulted in the formation of a macroemulsion. If atmospheric CO_2 was excluded by nitrogen blanketing, or if blending was done in a sealed system, the expected microemulsions resulted. The finished FRF emulsion may also be adversely affected if it is placed in an atmosphere of high CO_2 concentrations. Such problems occurred during several pour point measurements, where CO_2 evolved from the dry ice in the cooling bath leaked past the loose-fitting cork stopper and caused precipitate formation and phase separation in the FRF. It should be noted, however, that throughout this program, no phase stability problems have been encountered due to the CO_2 contamination during blending, storage, or handling of FRF in vented vessels.

Effects of Dust:

The effects of dust on FRF preparation and phase stability were investigated, using "fine" and "coarse" AC dust. Manufacturer's data on the particle size distribution of these dusts are given in Table 16.

Two sets of experiments were performed. In Set 1, the dust was predispersed in the base fuel before the addition of the other FRF components in order to simulate the effect of using a dirty fuel. In experimental Set 2, the dust

TABLE 16. PARTICLE SIZE DISTRIBUTION OF AC DUST

Size Range, Micrometers	AC Dust	
	Fine	Coarse
Below 5	39±2	12±2
5 to 10	18±3	12±3
10 to 20	16±3	14±3
20 to 40	18±3	23±3
40 to 80	9±3	30±3
80 to 200	----	9±3

was dispersed in the prefinished FRF. (The FRF comprised 84 vol% of base fuel No. 8821, 6 vol% of EA-8, and 10 vol% of water.) The amounts of dust dispersed in the total composition were 0, 50, 100, 500, and 1000 ppm. Experimental results confirmed predictions in that the,

- Finer dust gave more stable (hazier) dispersions than did the coarser dust;
- If the dust was predispersed in the base fuel prior to the addition of other components, it gave a more stable dust dispersion than if the dust was dispersed in the prefinished FRF due to high available surfactant concentration at the dust sites;
- Up to 100 ppm of either dust remained in the FRF invisible to the unaided eye. Higher concentrations of dust began to settle out of the FRF;
- No phase separation was observed in any of the studied cases.

Effects of Contaminant Particulates:

No problems have been encountered during this program which could be attributed to the presence of contaminants in base fuels. In fact, the presence of the emulsifier prevents the formation of precipitate which otherwise occurs in the referee-grade fuel (Code No. 7225). Base fuels with particulate contents ranging from nil to 13.5 mg/100 ml and accelerated stability total insolubles up to about 6 mg/100 ml have produced normal stable micro-emulsions.

Low-Temperature Properties of Fire-Resistant Diesel Fuel

To explore the low-temperature effects on FRF, a series of experiments was conducted using a device originally developed at SwRI for separating wax crystals from diesel fuels at low temperatures. (11) In this device, which is referred to as the "liquid-solid separator" (LSS), fuel is equilibrated at the test temperature while contained in a filtration chamber, in contact with a surface-type filter. Gas pressure is then applied, and the fraction of sample recovered as filtrate is noted. This device had been shown to be effective for detecting and separating wax-like crystals from distillate fuels at temperatures below the fuel freezing points. However, the water contained in FRF blends appears to clog the pores of the filter before the test can proceed when the test temperature is below about 0°C. This phenomenon possibly reflects a preferential wetting of the filter medium by water, leading to ice-filled pores at subzero (0°C) temperatures.

Frozen Fuel Detector Development:

To circumvent these observed difficulties, a modified apparatus was developed in which a 2- μ m filter rather than a 0.2- μ m filter is used to retain solids. Moreover, to prevent filter pore plugging with ice during chilling, the sample does not encounter the filter until temperatures have equilibrated and the test is initiated. To facilitate referring to this device while differentiating it from the former liquid-solid separator (LSS), it is referred to herein as the Frozen Fuel Detector (FFD). The device, illustra-

ted in Figure 11, consists of a sample reservoir cylinder connected via an on-off valve to a sintered metal depth-type filter, and a glass, graduated filtrate receiver. The stainless-steel sintered metal filter has a nominal pore size of 2 micrometers and an effective filtering area of 8.4 cm^2 . Some comparative data between the conventional LSS (with 0.22-micrometer pore size surface filter) and the FFD were obtained. These data, listed in Table 17, showed that the FFD filter does not plug with the FRF compositions at test temperatures of -0°C , whereas the conventional filter in the LSS does in many cases.

TABLE 17. COMPARISON OF PERFORMANCE OF THE FROZEN FUEL DETECTOR
(MODIFIED LIQUID-SOLID SEPARATOR)
WITH THAT OF THE ORIGINAL LIQUID-SOLID SEPARATOR

Base Fuel Type	Code No.	Surfactant/water Content, vol%/vol%	Min. vol% Passing Through Filter at -10°C	
			Liquid-Solid Sep.*	Frozen Fuel Det.**
DF-2	7225	0/0	96	99
		6/10	20	89
DF-1	9294	0/0	96	99
		6/10	3	91
DFA	9295	0/0	96	99
		6/10	14	90

* Prewetted $0.2 \mu\text{m}$ surface filter

** Precooled $2 \mu\text{m}$ sintered metal depth filter

Several series of experiments were conducted with the FFD, using DF-2, DF-1, and DF-A with various flow improver, and pour point depressant additives, and the results are summarized in Table 18. These data indicate that polyolefin-type polymers of 10^6 and 3×10^6 molecular weight do not significantly alter the formation of ice crystals in FRF at -10°C .

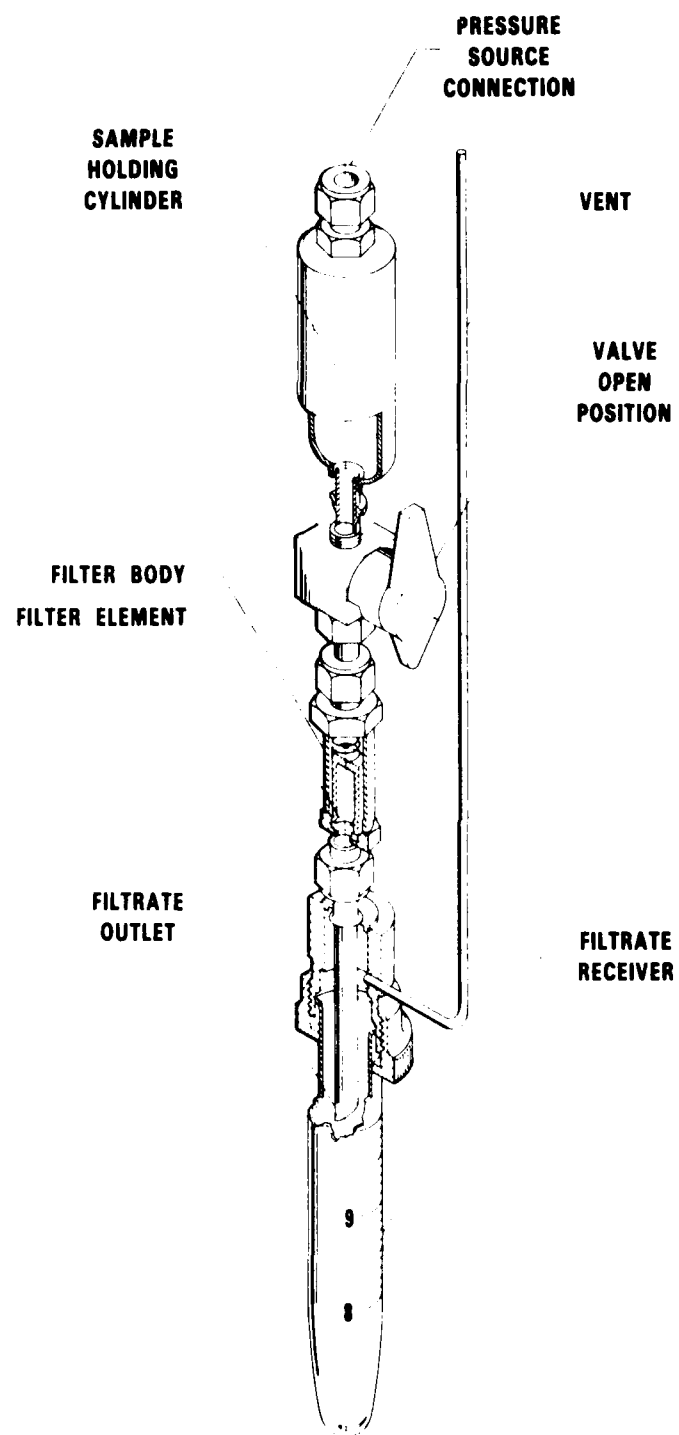


FIGURE 11. FROZEN FUEL DETECTOR

TABLE 18. SUMMARY OF DATA OBTAINED WITH FROZEN FUEL DETECTOR

Base Fuel		Temp, °C	Surfactant and Water Content, vol%/vol%	Flow Improver Additive		Vol% Passing Through Frozen Fuel Detector (Precooled 2 μ m Sintered Metal Depth Filter)
Type	Code No.			Name	Conc. wt%	
DF-2	7225	-10	----	---	---	99
		-30	----	---	---	64
		-30	----	Paradyne-25*	0.2	97
		-10	6/10	---	---	89
		-30	6/10	---	---	4
		-10	6/10	(10 ⁶ MW)**	0.2	87
		-10	6/10	(3x10 ⁶ MW)**	0.2	87
		-10	6/10	Paradyne-25	0.05	84-86
		-30	6/10	Paradyne-25	0.05	54-65
		-10	6/10	Paradyne-25	0.1	60
		-30	6/10	Paradyne-25	0.1	60-60
		-10	6/10	Paradyne-25	0.2	86-98
		-30	6/10	Paradyne-25	0.2	64-64
		-10	6/10	Paradyne-25	0.3	84
		-30	6/10	Paradyne-25	0.3	45
DF-1	9294	-10	----	---	---	99
		-30	----	---	---	99
		-10	6/10	---	---	91
		-10	6/10	(10 ⁶ MW)**	0.2	95
		-10	6/10	(3x10 ⁶ MW)**	0.2	91
		-10	6/10	Paradyne-25	0.05	94-95
		-30	6/10	Paradyne-25	0.05	14-16
		-10	6/10	Paradyne-25	0.1	92-94
		-30	6/10	Paradyne-25	0.1	10-10
		-30	6/10	Paradyne-25	0.2	62
		-10	6/10	Paradyne-25	0.3	96-96
		-30	6/10	Paradyne-25	0.3	96
DF-A	9295	-10	----	---	---	99
		-10	6/10	---	---	90
		-30	6/10	---	---	62-90
		-10	6/10	(10 ⁶ MW)**	0.2	95
		-10	6/10	Paradyne-25	0.05	95-95
		-30	6/10	Paradyne-25	0.05	48-71
		-10	6/10	Paradyne-25	0.1	93-98
		-30	6/10	Paradyne-25	0.1	10-35
		-10	6/10	Paradyne-25	0.2	95
		-30	6/10	Paradyne-25	0.2	97-99
		-30	6/10	Paradyne-25	0.3	62-62

* Proprietary flow improver additive manufactured by Exxon Chemicals, Inc.

** Proprietary commercial polyolefin polymer

The most extensive evaluation of additive effects involved the use of a commercial polymeric additive, Paradyne-25. The results demonstrate optimum additive concentrations of 0.2 and 0.3 wt% for DF-2 (or DF-A) and DF-1, respectively, where the filtrate yield is increased substantially in this static test.

Simulated Full-Scale Diesel Engine Fuel System:

The previously described studies of the low-temperature filterability of FRF with additives yielded promising results. Therefore, experiments were initiated to investigate the low-temperature flow performance of such FRF blends in a simulated diesel engine fuel system. These required the fabrication and assembly of a simulated DD6V-53T engine fuel system in a controlled temperature chamber. The system is shown in Figures 12 and 13. The assembled unit consists of DD6V-53T fuel pump, a primary filter (sock type in-depth), and a secondary (pleated paper) filter. The fuel tank (5 gallons), connecting tubings, and couplings are composed of No. 316 stainless steel for easy cleaning and leakproof performance under cyclic temperature conditions. Provisions are made to control (1) the recycle ratio by needle valves, (2) the pumping rate by variable speed DC motor, and (3) the recycle temperature. If needed in the future, a larger (25-gallon) tank could be easily installed in the chamber.

Preliminary experiments were conducted with the 6V-53T room temperature idle conditions of typical fuel consumption of 25 cm³/min and recycle of 1625 cm³/min. The system was filled with the test fuels at room temperature, and allowed to cool overnight to a set temperature. A DF-2 (No. 7225) base fuel and its FRF were tested to bracket the filter plugging temperatures. In case of the base fuel, these temperatures were between -18°C (no plugging for 20 minutes) and -22°C (no flow from start, complete plugging of primary filter). Corresponding temperatures for the FRF are -1° and -8°C, respectively.

Three base fuels, a DF-2 (No. 7225), a DF-1 (No. 9294), and a DF-A (No. 9295) and their FRF blends were evaluated under the dynamic conditions of

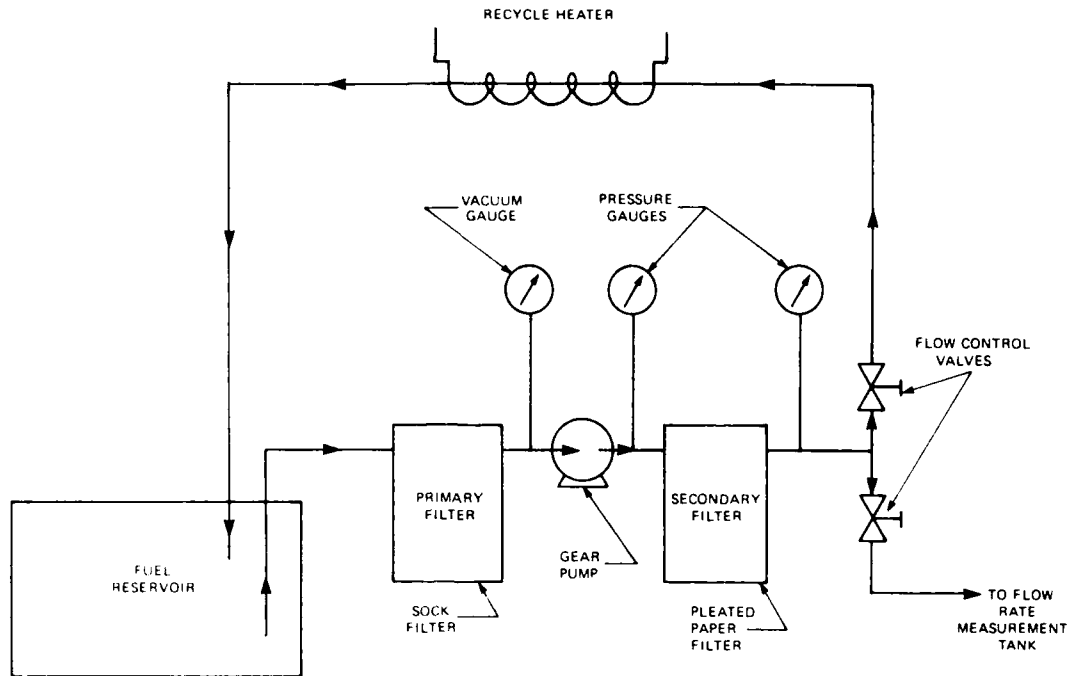


FIGURE 12. FLOW DIAGRAM OF SIMULATED DD6V-53 ENGINE FUEL SYSTEM

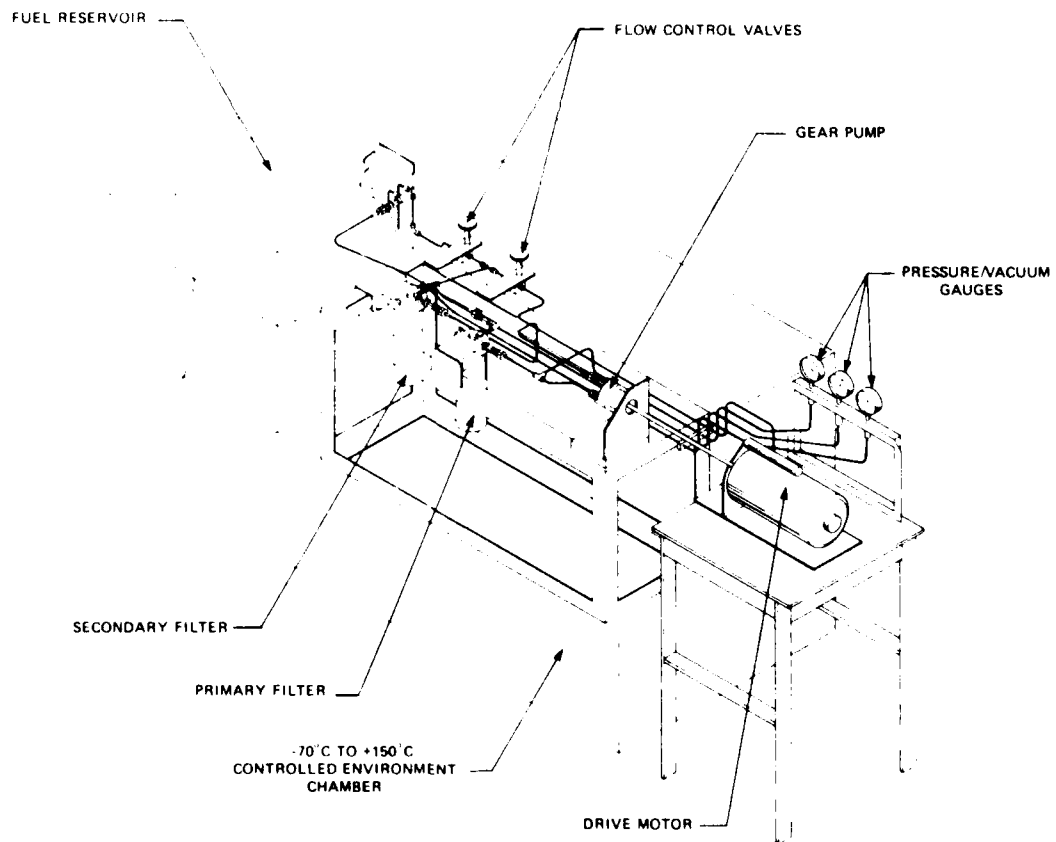


FIGURE 13. ILLUSTRATION OF CONTROLLED-TEMPERATURE DD6V-53 ENGINE FUEL SYSTEM SIMULATOR

full recycle while temperatures dropped continuously. The system was filled at room temperature with 5 gallons of fuel, and idle speed was set to give 1650 ml/min flow totally recycled to the fuel tank. The chamber air, and thus the fuel tank, temperature was then allowed to drop continuously until the filter plugged. In all cases, the primary sock-type filter became plugged and caused cavitation as evidenced by a drastic drop in the pump outlet pressure and rise in the pump outlet vacuum. The results of the tests are summarized in Table 19.

TABLE 19. LOW-TEMPERATURE FILTERABILITY OF FRF AND BASE FUELS
DETERMINED IN SIMULATED DD6V-53T ENGINE FUEL SYSTEM

Sample	Temperatures (°C) At Filter Plugging	
	Fuel In Tank	Chamber Air
DF-2* (7225)	-20	-31
FRF OF DF-2* (84 Vol% 7225 + 6 Vol% EA-78 + 10 Vol% Water)	-2	-12
DF-1* (9294)	-32	-36
FRF of DF-1* (84 vol% 9294 + 6 vol% EA-78 + 10 vol% water)	+8	-8
DF-A* (9295)	-53	-72
FRF of DF-A* (84 vol% 9295 + 6 vol% EA-78 + 10 vol% water)	0	-16

*Properties of Base Fuels

	<u>Pour Point, °C</u>	<u>Cloud Point, °C</u>
AL-7225-F	-24	-21
AL-9294-F	-36	-23
AL-9295-F	-56	-52

Under the conditions described, the filter-plugging temperatures for the three base fuels are 2° to 4°C above their pour points. The filter-plugging temperature for all the FRF's appear to be very near 0°C. It should be noted that for dynamic conditions, the chamber air temperature was approximately 15°C below the temperature of the fuel in the tank. Therefore, some parts (e.g., filter canisters) of the system may have been cooler than the fuel in the tank. A multipoint automatic scanning and logging system was then installed to record temperatures of all components and pressures at critical points.

A series of experiments was conducted in this system in which effects of additives on the filter plugging temperature of FRF made with DF-2 were evaluated, and the results are summarized in Table 20. Additives included the commercial polymeric additive, Paradyne-25, at 0.01 to 0.2 wt%; ethylene glycol at 4 to 9 vol%; triethylene glycol at 1 to 5 vol%; ethylene glycol monomethyl ether (EGME or 2-methoxyethanol) at 5 vol%; ethylene glycol dimethyl ether (EGDME or dimethoxyethanol) at 1 to 5 vol%; diethylene glycol monomethyl ether (DEGME or 4-methoxy n-butanol) at 5 vol%; and ethylene glycol monomethyl monoethyl ether or [1,2-bis(2-methoxyethoxy) ethane] at 1 to 5 vol%. None of these experiments demonstrated filter plugging temperatures below -2° to -5°C.

FRF Quality Assurance Methodology

Various means for monitoring FRF quality have been considered during the course of the FRF development program, and some of these have been subjected to limited experimental evaluation. A search of the literature for methods for measuring water content of FRF has been conducted, and various approaches have been considered and/or investigated. Computerized literature searches of Chemical Abstracts (CA), National Technical Information Service (NTIS), and American Petroleum Institute were made. Key words were water, diesel, analysis. Only two references of any significance were found, both Russian.

TABLE 20. LOW-TEMPERATURE FILTERABILITY OF MODIFIED FRF
DETERMINED IN SIMULATED DD6V-53T ENGINE FUEL SYSTEM

Sample	Temperature at Filter Plugging, °C		
	Fuel in Tank	Fuel in Filter	Chamber Air
FRF of DF-2	-2	-1	-11
(84 vol% 7225 + 6 vol% EA-78 + 10 vol% water)	-4	-3	-16
<u>FRF OF DF-2</u>			
<u>With Wax-Crystal Modifier</u>			
FRF of DF-2 + 0.01 wt% Paradyne-25*	-3	-3	-14
FRF of DF-2 + 0.05 wt% Paradyne-25*	-4	-3	-15
FRF of DF-2 + 0.2 wt% Paradyne-25*	-4	-3	-9
<u>FRF of DF-2 With</u>			
<u>Ethylene Glycol</u>			
79 vol% 7225 + 7 vol% EA-99 + 10 vol% Water + 4 vol% Ethylene Glycol	-2	-2	-9
79 vol% 8825 + 7 vol% EA-99 + 10 vol% Water + 4 vol% Ethylene Glycol	-3	-4	-17
76 vol% 7225 + 6 vol% EA-78 + 9 vol% Water + 9 vol% Ethylene Glycol	-5	-5	-10
<u>FRF of DF-2 with Tri</u>			
<u>Ethylene Glycol (TEG)</u>			
83 vol% DF-2 + 6 vol% EA-99 + 10 vol% Water + 1 vol% TEG	-4	-4	-14
79 vol% DF-2 + 6 vol% EA-99 + 10 vol% Water + 5 vol% TEG	-3	-3	-10
<u>FRF of DF-2 with Ethylene</u>			
<u>Glycol Monomethyl Ether</u>			
<u>(EGME) 79 vol% DF-2 +</u>			
<u>6 vol% EA-99 + 10 vol%</u>			
<u>Water 5 vol% EGME</u>			
	-3	-4	-12

* Proprietary commercial flow improver additive manufactured by Exxon Chemicals, Inc.

TABLE 20. LOW-TEMPERATURE FILTERABILITY OF MODIFIED FRF
DETERMINED IN SIMULATED DD6V-53T ENGINE FUEL SYSTEM (CONT'D)

<u>Sample</u>	<u>Temperature at Filter Plugging, °C</u>		
	<u>Fuel in Tank</u>	<u>Fuel in Filter</u>	<u>Chamber Air</u>
<u>FRF of DF-2 with Ethylene</u>	-5	-4	-10
<u>Glycol Dimethyl Ether (EDGME)</u>			
83 vol% DF-2 + 6 vol% EA-99			
+ 10 vol% Water + 1 vol% EGDME			
79 vol% DF-2 + 3 vol% EA-99	-3	-4	-11
+ 3 vol% SOA** + 10 vol% Water			
+ 5 vol% EGDME			
<u>FRF of DF-2 with Diethylene</u>	-4	-4	-20
<u>Glycol Monomethyl Ether (DEGME)</u>			
79 vol% DF-2 + 3 vol% EA-99			
+ 3 vol% SOA** + 10 vol% Water			
+ 5 vol% DEGME			
<u>FRF of DF-2 with 1, 2, Bis(2-</u>	-4	-4	-13
<u>methoxy Ethoxy) Ethane</u>			
83 vol% DF-2 + 6 vol% EA-99			
+ 10 vol% water + 1 vol% 1-2 Bis			
(2-methoxy ethoxy) ethane			
79 vol% DF-2 + 6 vol% EA-99	-3	-4	-10
+ 10 vol% water + 5 vol% 1-2 Bis			
(2-methoxy ethoxy) ethane			

** Proprietary emulsifier manufactured by Scher Chemicals, Inc., Clifton, N.J.

RAPID MEASUREMENT OF THE WATER CONTENT IN PETROLEUM AND PETROLEUM PRODUCTS USING MILLIMETER-WAVE MOISTURE METERS, Dem'Yanov, A.A.; Papko, V.V.; Vinogradov, V.M. Mosk Inst. Neftekhim. Gazov Prom. IM. Gubkina, Moscow, USSR Zavod. Lab., 73, 39(10), 1209-12, Coden: Zvdlaa

DEVICE FOR DETERMINING WATER CONTENT IN PETROLEUM PRODUCTS IN A FLOW, Ya.M.; Spirin, A.A.; Salaev, G.SH. Azerb. Inst. Nefti. Khim. IM. Azizbekova, Baku, USSR IZV. Vyssh. Ucheb. Zaved., Neft Gaz, 71, 14(6), 88-90, Coden: Ivuna.

It is believed that these references refer to microwave devices. Translations have been ordered, but none has yet been received. The limited success of the computer search could probably have been anticipated, since there was little need for analysis of this type prior to the FRF concept.

The following paragraphs discuss some possible analytical approaches and describe results of investigations in these areas.

Category A--Separation of Phases:

Extraction (by breaking emulsion) -- A series of commercially available demulsifiers was examined for their effects on the FRF microemulsions, with the expectation that they may break these emulsions, and the separated water could be measured in a graduated vessel. A total of eleven such demulsifiers was tested at concentration of 5 vol% in the FRF blend. Simple mixing of the ingredients, followed by an overnight settling period, did not produce the required results. Centrifuging of these samples at 1000 rpm for 30 minutes, however, gave promising results with one of the demulsifiers. In this sample, 9 vol% of white "cream" separated at the bottom of the centrifuge tube and was topped with a very hazy upper layer. Three other demulsifiers produced separated bottom layers amounting to between 25 to 40 vol%, while the remaining additives were ineffective.

A "salting out" procedure, using a large excess of electrolyte, i.e., magnesium nitrate, resulted in instant macroemulsion formation; however, more than an hour of centrifuging was needed at about 1000 rpm before over 90 percent of the water had separated as a milky liquid. Addition of ethylene glycol resulted in still poorer separation of the water from the aqueous fuel microemulsion.

Use of an ultra centrifuge and alternate demulsifiers may possibly produce a simple method. The complete separation of phases could be very difficult; however, this approach deserves further investigation.

Distillation -- Extreme bumping and foaming portend substantial problems. This process does not appear to be promising.

Category B--Reactions

Karl Fischer Method -- This method is presently being used in the laboratory with good results to determine water in FRF. This is the only established method to date.

Reactions with water to produce unique compounds -- An example could be reaction of calcium carbide with water to produce acetylene. Such reactions for this purpose, have not been investigated as part of this program.

Reaction/adsorption of water to generate heat -- Attempts to remove water with silica gel were unsuccessful due to poor contact between silica and water. Use of ultrasonics could possibly improve contact.

A new, promising procedure to determine water content has recently been developed by Mobil Research and Development Corp.* under contract to the U.S. Bureau of Mines. The principle of operation is the measurement of the heat of adsorption generated when a water emulsion is injected onto a zeolite adsorbent. This work was conducted with hydraulic fluids containing

*Private communications with Dr. D. Law, Mobil Research and Development Corp.

40 to 50 percent water; however, it was anticipated that this same procedure could be used to determine water concentration in the range used in FRF formulations.

In order to evaluate this procedure, a series of four samples was sent to Mobil for evaluation. The following results were supplied, courtesy of Mobil:

Sample	Water Content, wt%	
	Karl Fischer	Heat of Adsorption
(1) Neat Fuel	0.03	< 0.5
(2) Neat + 6% Surfactant	----	< 0.5
(3) Neat + 3% Sur. + 5% Water (vol)	6.13	6.2, 6.0
(4) Neat + 6% Sur. + 10% Water (vol)	11.97	11.5, 11.8, 11.8

Based on these cursory results, further evaluations were conducted in this laboratory with an apparatus borrowed from Mobil.

The results of these latter experiments indicated that a quantitative method for the measurement of water content could probably be developed. However, the procedure was considered to be too time consuming for practical use in FRF field applications.

Category C--Physical Measurement:

UV, Visible, IR Spectroscopy -- These methods would measure the organic content and determine water by difference. Haze in actual emulsion would have to be eliminated (by appropriate solvent). These methods do not currently look promising. On the other hand, the use of visible spectra as a quality assurance method for quantitatively describing the appearance (haziness) does appear to be feasible. This approach was extensively investigated in this laboratory, and the results are discussed in the following paragraphs.

To describe objectively the appearance and thereby the quality of micro-emulsifications, their visible spectra were measured between 400 and 800 nm

wavelengths. Representative FRFs were made that contained 10 vol% water and 3 to 10 vol% of surfactant in 27 different diesel fuels. In the spectrophotometer's reference cell, the composition was identical to that of the sample cell, but the water was replaced by n-hexadecane or i-octane. The resultant absorbance data were, therefore, due to water-caused haziness. The same experiments were repeated, but 6 vol% of the base fuel was replaced by the same amount of aromatic concentrate. In each case where the compositions were transparent through 25-mm pathlength, similar to sample No. 6 of Figure 8, the absorbance at a wavelength of 450 nm was equal to or less than 0.5 through a 10-mm cell. Hazier composition, similar to Sample No. 4 of Figure 8, exhibited absorbance values between 0.5 and 0.9 under identical conditions. These sets of visible spectra are given in Figures 14 and 15.

These data may serve as basis for a quality assurance "black box" type equipment. The 100 gal./hr (and future) FRF blending unit premixes the fuel with the surfactant, and to this premix, it adds the water to produce FRF. It would be easy to divert some of the final deaerated FRF blend to the sample side, and the fuel-surfactant premix into the reference side of a simple, fixed wavelength absorbance detector. If this detector senses that the absorbance is below 0.5, it means that the product is an almost clear microemulsion, while if the absorbance is between 0.5 and 1.0, the FRF would be a hazy, but still acceptable microemulsion. Any absorbance higher than 1.0 would signal that the product is not a stable microemulsion.

In a third set of experiments, the visible region spectra of selected formulations with a "visible rating of 1" (translucent microemulsion) were measured, with nothing but air in the path of the reference beam. Within the limits imposed by the relatively small number of data points, it may be concluded absorbance values were about 0.7 at 550 nm, and below 0.3 at 600 nm. A "black box" measuring device based on this principle would be the simplest unit.

Nuclear Magnetic Resonance (NMR)--A commercially available instrument based on "echo NMR" is used primarily to determine water in foods. This device was not available for evaluation for the present application.

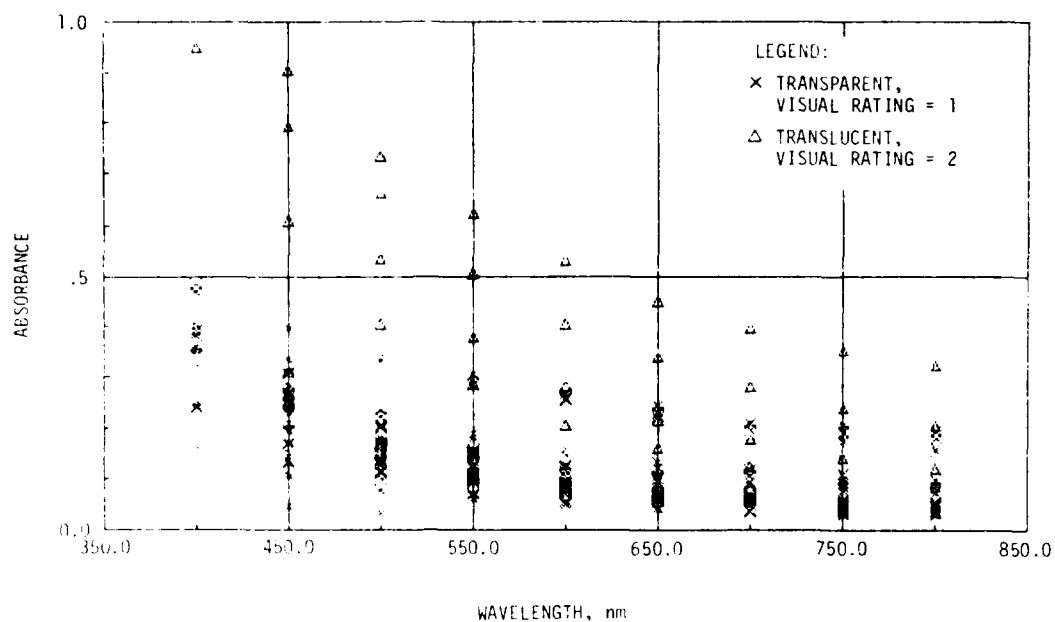


FIGURE 14. VISIBLE REGION SPECTRA OF AQUEOUS MICROEMULSIONS WITH VISUAL RATING OF "1" AND "2" IN VARIOUS AROMATIC CONCENTRATE-CONTAINING DIESEL FUELS

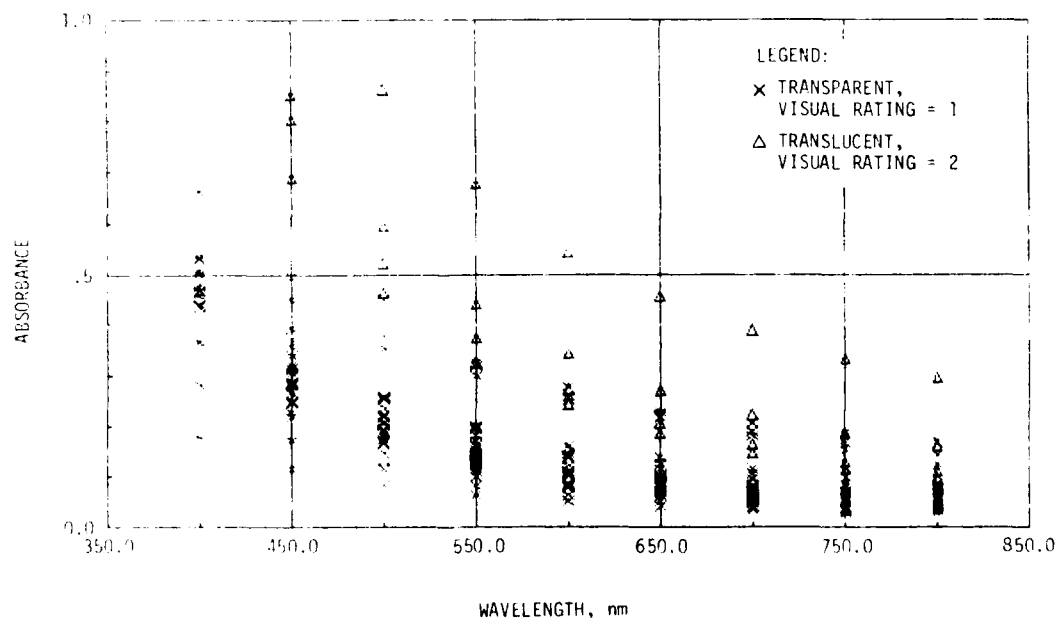


FIGURE 15. VISIBLE REGION SPECTRA OF AQUEOUS MICROEMULSIONS WITH VISUAL RATING OF "1" AND "2" IN VARIOUS AROMATIC CONCENTRATE-CONTAINING DIESEL FUELS

The amplitudes and the amplitude ratios of the FID and the two pulse echoes were significantly different as may be seen from the data in Table 21.

TABLE 21. TRANSIENT NMR DATA FOR AN FRF AND ITS COMPONENTS

Sample	FID (A)	Relative Amplitude		Ratio of Amplitudes	
		Echo at 50 ms. (B)	Echo at 100 ms. (C)	B/A	C/A
1	13.4	9.4	5.1	0.543	0.381
2	14.4	0.6	0.04	0.067	0.003
3	13.6	8.8	4.7	0.534	0.346
4	13.2	9.6	5.6	0.583	0.424

The ratio (C/A) of the echo amplitude (C) at 100 milliseconds relative to the FID amplitude (A) provides a positive indication of the presence of water in sample No. 4 compared to sample No. 3. The basis for this difference is the longer T_2 , the spin-spin relaxation time, of the water compared to the other constituents. If this condition holds over the range of constituent variables and temperatures of interest, then the transient NMR method can be useful for measurement of the water content in fire-resistant fuels. On the basis of experience with other materials, there is reason to believe that this will be the case. However, it should be verified in a more extensive laboratory study as should the level of accuracy that can be achieved. The optimum echo time may be different from 100 milliseconds, and this also needs to be determined. If positive results are obtained, then the implementation of the approach for on-stream monitoring could be readily accomplished and should be relatively inexpensive.

Differential Thermal Analysis/Thermogravimetric Analysis (DTA/TGA)--No information is available as to the degree of success that might be attained.

Gas Chromatography (GC)--Analysis could be done by GC, but practical considerations probably preclude any real success with this approach.

High Pressure Liquid Chromatography (HPLC)--Same as above item.

Calorimetry--For use with preceding three methods.

Electrical Conductivity -- Not promising because water is the internal phase.

Thermal Conductivity -- No information relative to this application is available.

Dielectric Constant -- Initial laboratory evaluations indicate some potential if sensitivity could be improved.

A fully automatic LCR meter (Inductance, Capacitance, Resistance) was utilized to measure dielectric constant of the water-in-oil emulsions. The detector was a gold-plated annular capacitor (15 mm ID of outer tube x 12 mm OD of inner tube x 80 mm long with a nominal air capacitance of 34.5 pF) in contact with the fuel at 25°C. The results of the measurements are presented in Tables 22 through 25. The effect of aging of the emulsion on the dielectric constant is summarized in Table 22.

TABLE 22. TYPICAL EFFECTS OF AGING ON DIELECTRIC
CONSTANT OF W/O EMULSIONS
(Wetted Capacitor)

Composition Parts by Volume Fuel/EA/Water 8821/78/H ₂ O	Age of Emulsion, Hours (after preparation)	Dielectric Constant at 25°C Test Frequency		
		10 kHz	1 kHz	120 Hz
84/7/9	3	4.887	5.217	5.536
	20	3.449	3.554	3.565
	192	3.365	3.466	3.507
83/6/11	26	3.438	3.557	3.623
	125	3.299	3.386	3.449
	144	3.258	3.391	--
	171	3.238	3.351	3.594
86/5/9	25	3.142	3.235	3.304
	190	3.093	3.200	3.391

The data indicate that the dielectric constant at all test frequencies decreases as age of the emulsion increases; and that the dielectric constant slightly increases at lower test frequencies.

Table 23 presents the effect of water concentration on the dielectric constant. The ratio of fuel-to-surfactant volumes for this series was constant at 84:6. The dielectric constant was maximum at 2 parts by volume water, decreased rapidly as water content increased to 6 parts. The change in the dielectric constant with water content between 7 and 10 parts was insignificant. The effect of increasing surfactant concentration on the dielectric constant with a constant fuel/water ratio in emulsions is presented in Table 24. The changes in the dielectric constants vary slightly between 3 and 6 parts surfactant; however, the change in the dielectric constant is very rapid beyond surfactant concentrations of 7 parts by volume. Table 25 presents the dielectric constant values of FRF compositions with surfactant variations between 5 and 7 and water variations between 9 and 11.

TABLE 23. EFFECT OF WATER CONTENT ON DIELECTRIC CONSTANT
OF W/O EMULSION
(Wetted Capacitor)

Composition Parts by Volume Fuel/EA/Water 8821/78/H ₂ O	Age of Emulsion, Hours (after preparation)	Dielectric Constant at 25°C
		Test Frequency 10 kHz
100/0/0	--	2.058
84/6/0	80	2.661
84/6/1	96	4.310
84/6/2	96	4.808
84/6/3	96	4.496
84/6/4	120	3.948
84/6/5	120	3.696
84/6/5	1450	3.000
84/6/6	120	3.394
84/6/7	120	3.186
84/6/8	144	3.171
84/6/9	144	3.168
84/6/9	1470	3.078
84/6/10	144	3.200
84/6/10	1470	2.983

TABLE 24. EFFECT OF EMULSIFYING AGENT ON DIELECTRIC CONSTANT
OF W/O EMULSIONS
(Wetted Capacitor)

Composition Parts by Volume Fuel/EA/Water 8821/78/H ₂ O	Age of Emulsion, Hours (after preparation)	Dielectric Constant at 25°C	
		Test Frequency	
		10 kHz	
84/1/10 ²	144	2.693	
84/2/10	144	2.977	
84/3/10	144	3.023	
84/4/10	170	3.078	
84/5/10	170	3.186	
	720	3.125	
	740	3.124	
	744	3.085	
84/6/10	170	3.380	
	720	3.157	
	740	3.125	
84/7/10	170	4.122	
84/8/10	170	5.623	
84/9/10	170	7.101	
84/10/10	170	10.783	

TABLE 25. DIELECTRIC CONSTANT OF NEAR-FRF COMPOSITIONS

Composition Parts by Volume Fuel/EA/Water 8821/78/H ₂ O	Age of Emulsion, Hours (after preparation)	Dielectric Constant at 25°C		
		Test Frequency		
		10 kHz	1 kHz	120 Hz
86/5/9	190	3.093	3.200	3.391
	124	3.096	3.171	3.217
85/5/10	100	3.191	3.391	3.391
	200	3.440	3.545	3.652
84/5/11	220	3.310	3.388	3.450
	245	3.464	3.557	3.623
85/6/9	264	3.345	3.441	3.507
	270	3.159	3.249	3.304
84/6/10	250	3.261	3.362	3.423
	310	3.183	3.275	3.333
83/6/11	260	3.255	3.354	3.423
	280	3.064	3.133	3.188
84/7/9	300	3.426	3.536	3.580
	315	3.542	3.674	3.739
83/7/10	300	3.588	3.738	3.797
	340	3.507	3.626	3.680
82/7/11	290	3.548	3.678	3.739
	310	3.249	3.325	3.362

Subsequently, a series of experiments was conducted with a 100 mm x 100 mm parallel plate capacitor formed on the outside surface of a rectangular borosilicate glass cuvette with 150 mm x 150 mm x 14 mm outside dimensions and 3-mm glass thickness. The results of dielectric measurement on FRFs with this capacitor are summarized in Table 26. In this series, the fuel-to-surfactant volume ratio was kept constant at 84:6, and the water content was varied from 7 to 11 parts by volume.

TABLE 26. DIELECTRIC CONSTANT OF FRF COMPOSITIONS
(Parallel Plate Capacitor)
(Fuel in Contact with Pyrex)

Comp. Parts by Vol Fuel/ EA/Water <u>84/21/78/H₂O</u>	Appx Age of Separate Samples (Hr after prep.)	Dielectric Constant at Test Frequency		
		120 Hz	1.0 kHz	10.0 Hz
100/0/0	----	2.049	1.921	1.903
		2.049	1.921	1.902
84/6/0	24	13.555	11.292	3.158
	72	13.444	11.421-11.434	3.265
	192	13.316	11.268-11.255	3.226
84/6/7	24(1)	7.8(1)	5.051	4.783
	48	7.939-8.194(2)	4.776-4.673	4.507-4.392
	168	8.579-8.835	4.148-4.085	3.841-3.752
84/6/8	24	7.545	4.923	4.65
	48	7.682-7.81	4.673-4.584	4.405-4.302
	168	8.323-8.579	3.995-3.918	3.675-3.585
84/6/9	24	7.417	4.731	4.475
	48	7.554-7.682	4.405-4.251	4.136-3.982
	168	8.195-8.323	3.816-3.764	3.508-3.444
84/6/10	24	7.033	4.783	4.539
	48	7.554-7.554	4.251-4.161	3.982-3.905
	168	7.938-8.067	3.688-3.649	3.406-3.355
84/6/11	24	6.905	4.673	4.443
	48	7.042-7.170	4.199-4.174	3.956-3.918
	168	7.682-7.81	3.611-3.572	3.342-3.303

Notes:

1. Dielectric measurements recorded 5 minutes after sample was transferred into capacitor cell--all 24-hour aged samples.
2. Dielectric constants separated by a dash are measurements at 1 minute and 60 minutes after sample was transferred into capacitor cell.

The results of this investigation indicate that, at the excitation frequencies used in these experiments, the dielectric constant does not represent a suitable measure of water content in the concentration ranges typical of FRF.

Microwave -- This process could have possibilities. The simplest such method would be based upon microwave dielectric loss measurement to monitor the water content of these emulsions. Microwave dielectric loss at a frequency of about 23 to 24 GHz is specific for water; however, the loss at this frequency may be so high that it might not be practical to make the pathlength small enough. From the literature, it appears that pure water attenuates microwaves more moderately at 2550 MHz, used in microwave ovens. Hence, the latter frequency may be appropriate for use in an analytical instrument based on a simple flow-through cell provided with appropriate electronic components for measuring thermistor resistance changes as a function of water concentration. Such an instrument, operating at a different wavelength, may be suitable for measuring surfactant content also.

Full-Scale Ballistic Tests of Armored Vehicular Fuel Tanks

In support of the Army fire-resistant diesel fuel development program, a series of full-scale ballistic tests was arranged for by AFLRL under a separate contract from MERADCOM* to be conducted at New Mexico Institute of Mining and Technology. The purpose of these tests was to establish whether or not the self-extinguishing property of FRF would prove effective in a realistic combat-type environment. The tests utilized 3.2-inch precision shaped charges fired through the armor and internally mounted fuel tanks of M48 and M113 armored personnel carrier hulks, in which the fuel was heated to 77°C. Warheads were obtained by MERADCOM, and AFLRL personnel participated in the planning and conducting of the tests.

*Wright, B.R., and Weatherford, W.D., Jr., "Investigation of Fire-Vulnerability-Reduction Effectiveness of Fire-Resistant Diesel Fuel in Armored Vehicular Fuel Tanks", AFLRL Final Report No. 130, Defense Documentation Center No. AD A055058, 1980 [Contract No. DAAK70-79-C-0215].

Results confirmed that residual burning can be eliminated by the use of FRF even though the base fuel flash point is 25°C lower than the test temperature and the transient fireball development is similar to that of neat fuel. Instrumentation response indicated that pressure effects are not affected by FRF but that sustained temperatures are drastically reduced by the FRF self-extinguishment.

III. BASIC RESEARCH ON FRF FLAMMABILITY MITIGATION MECHANISMS

A new phase of the Army's FRF development program was initiated during the period of performance covered by this report. The purpose of this phase has been to conduct basic research on the influences of FRF composition, physical properties, flammability characteristics, and imposed conditions on the mechanisms of flammability mitigation which function in such fuels.

As previously noted, diesel fuel containing water dispersed as a water-in-fuel emulsion (FRF) exhibits diminished mist flammability and produces rapid self-extinguishment of flaming bulk liquid surfaces. Improved understanding of flammability mitigation mechanisms which function in such fuels and the influences of fuel variables thereon is needed to facilitate development of optimum FRF formulations.

Objectives

Specific objectives of this research have included:

- Conduct a survey of current and/or prior research pertinent to the stated objectives. This survey includes consultation with investigators at academic institutions who are studying the formation and properties of water-in-fuel emulsions.
- Develop and/or adapt research facilities for studying flammability mitigation mechanisms which past or current research has not addressed or has not confirmed.
- Investigate interrelations among dominant mechanisms. Specific mechanisms to be addressed include:
 - Physical inhibition of preflame and flame reactions by dilution with water vapor;

- Phase rule restrictions for immiscible phases which would limit maximum surface temperatures to the boiling point of water; and
- Cooling by evaporation of water, which is more volatile than the base fuel, to yield surface temperatures substantially less than the boiling point of water.

Survey

The survey was initiated with visits to the laboratories of Northwestern, Drexel, and Princeton Universities. The results of these consultations were interpreted by this laboratory as confirmation that the mechanisms by which water-in-fuel microemulsions exhibit diminished mist flammability and self-extinguishment of pool burning had not yet been adequately explained.

Experimental Approach

During the period of performance covered by this report, three different sets of experiments have developed data which quantitatively correlate (1), measured FRF vapor compositions with (2), experimental flammability limits and (3), observed horizontal flame propagation phenomena. These experiments and their results are described in the following sections of this report.

Experimental Studies

The first area selected for study was the dilution effect of water vapor in suppressing the flammability of combustible fuel/air mixtures. Other studies have shown that methane/air mixtures containing water vapor have reduced flammability and flame speed. While data are available on the effect of water vapor in some of the low-molecular weight hydrocarbon/air mixtures, no data are available on the heavier hydrocarbons common to middle distillate fuels.

An experimental apparatus was assembled to measure the effect of water vapor dilution on the flammability of hydrocarbon-air mixtures. Briefly, the apparatus, which is illustrated in Figures 16 and 17, consists of a heated

bomb equipped with transducers and thermocouples to measure static pressure and temperature, respectively. Vacuum generation is provided for pump-down to dispose of gases from previous experiments; for induction of water vapor from a separately controlled, heated water reservoir; for induction of the vapor from a separately controlled, heated fuel reservoir; and for induction of conditioned air to achieve the desired total pressure for each experiment. The tube which brings the reactants into the bomb is designed to create swirl to assure adequate mixing. Fuel and water are admitted to the bomb as gases through heated lines, and concentrations are determined by measuring the partial pressure of each component as it is added. The entire system is kept at a constant temperature of approximately 90°C to prevent condensation of fuel or water vapors. A high-voltage spark provides an overwhelming ignition source within the bomb, and flame propagation is detected by a pressure rise in the system.

The flammability measurements were performed at atmospheric pressure, so immediately prior to ignition, the air inlet tube was opened. A pressure rise in the bomb was accompanied by an abrupt issuance of gas from the air inlet tube. This was detected by placing a very small metal foil cup over the vertically oriented air inlet tube. The most minute gas flow from the bomb would tip the cup and indicate flame propagation. This air inlet tube was a capillary with an ID of about one millimeter so there was no possibility of the composition changing in the bomb in the short time (≈ 2 sec) that it was open before ignition. This method of detecting pressure rise was much more sensitive than a transducer would have been which could cover the wide range of pressure rises encountered in these experiments.

For low-boiling hydrocarbon fractions, the heated fuel reservoir can be used to supply to the bomb a vapor mixture which has been equilibrated at pre-selected conditions of temperature and vapor-liquid ratio. However, in the case of the diesel fuels of interest to this study, it proved difficult to generate sufficient vapors to achieve the desired fuel partial pressures in the bomb. Consequently, as an alternative approach, 1 vol% of each of the three different diesel fuels to be studied was distilled at zero reflux to yield a totally vaporizable fraction for use in the flammability limits

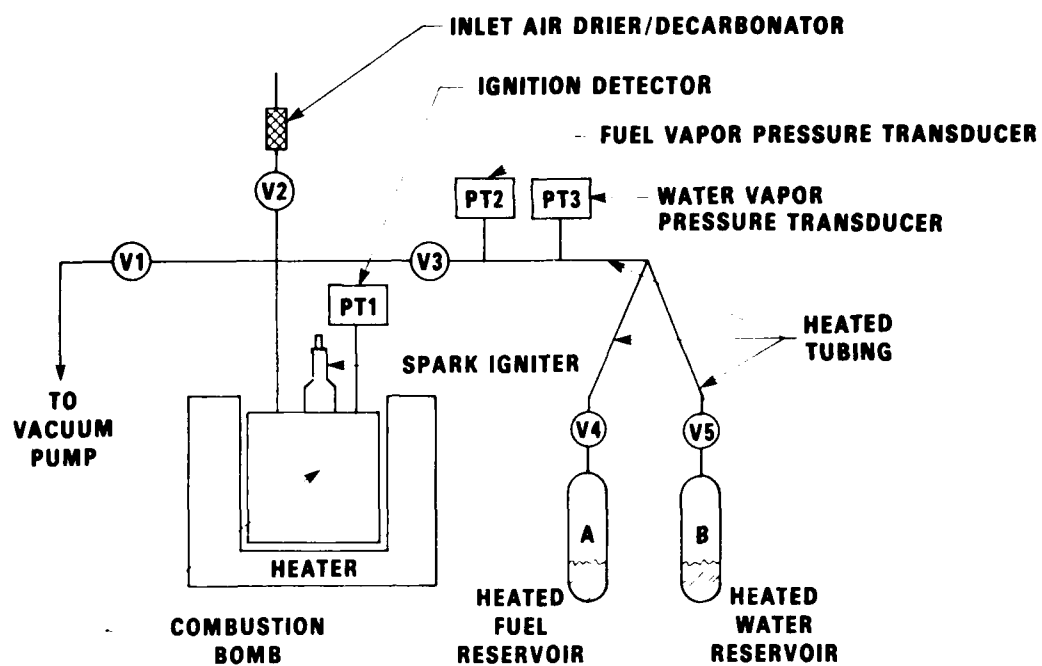


FIGURE 16. ILLUSTRATION OF FLAMMABILITY LIMITS APPARATUS

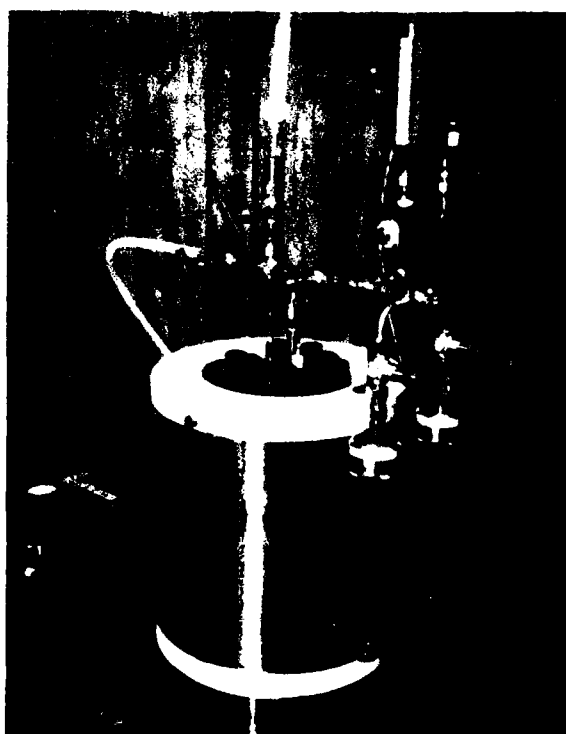


FIGURE 17. PHOTOGRAPH OF FLAMMABILITY LIMITS APPARATUS

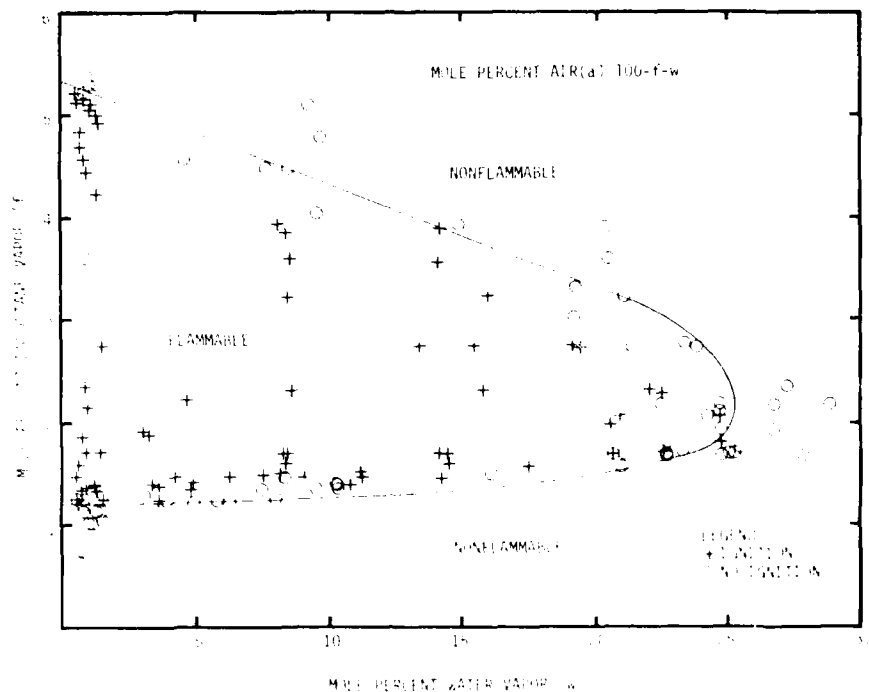


FIGURE 18. FLAMMABILITY DIAGRAM FOR ISOCTANE VAPOR

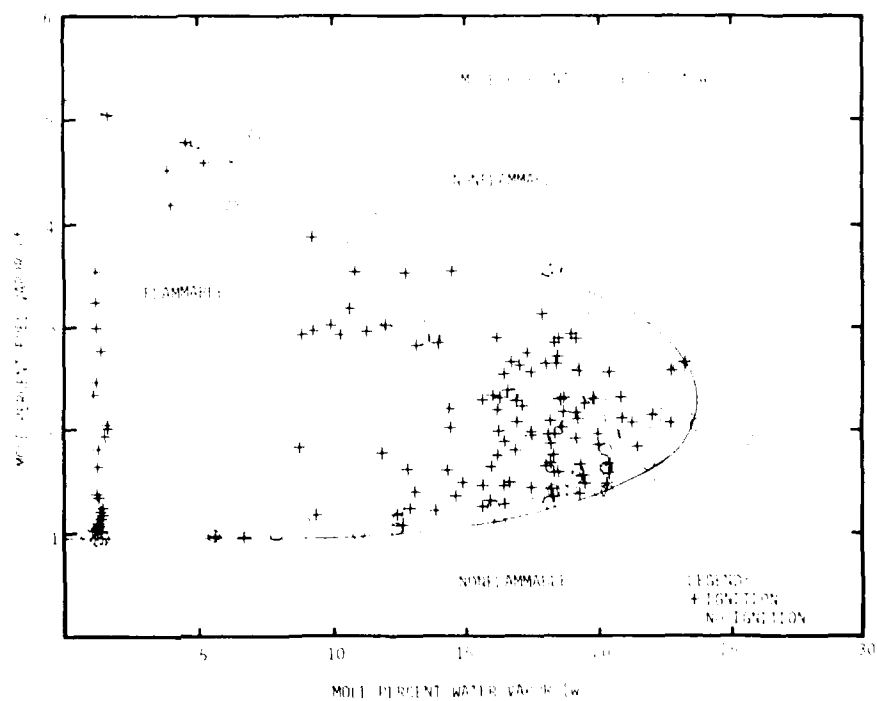


FIGURE 19. FLAMMABILITY DIAGRAM FOR 45°C FLASH POINT DIESEL FUEL VAPOR

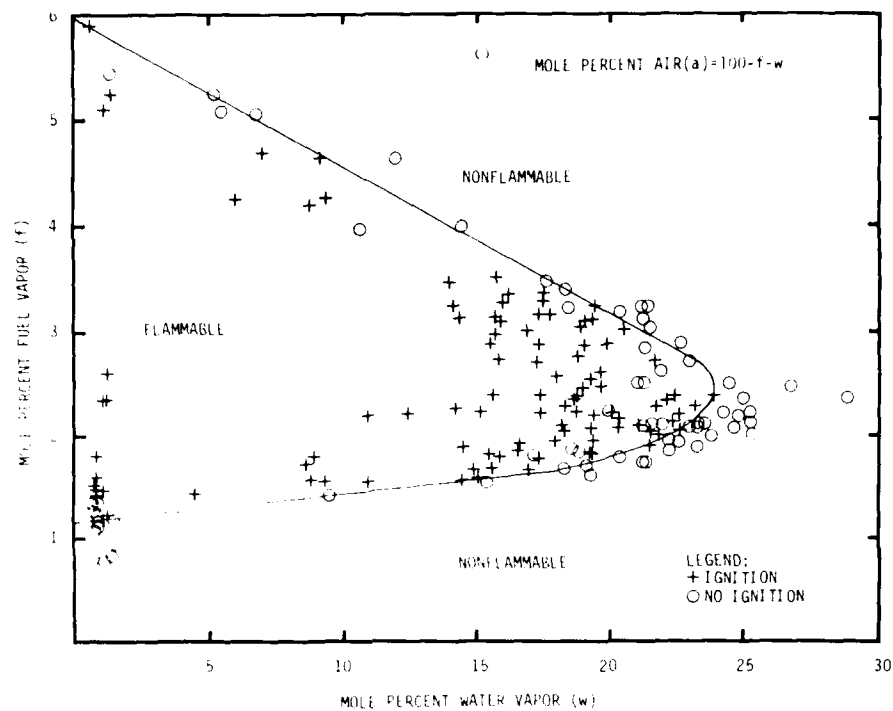


FIGURE 20. FLAMMABILITY DIAGRAM FOR 60°C FLASH POINT DIESEL FUEL VAPOR

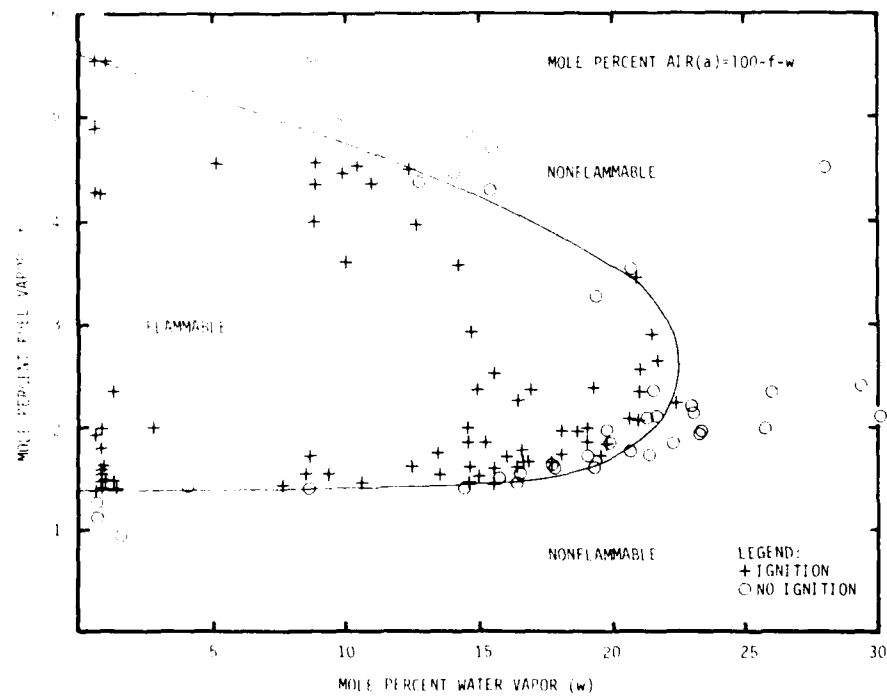


FIGURE 21. FLAMMABILITY DIAGRAM FOR 72°C FLASH POINT DIESEL FUEL VAPOR

apparatus. Analyses of these fractions and of vapors evolved from the total fuels at the flash point temperature indicate that composition differences among the 1% fractions are representative of flash point upper composition differences. These three base fuels, Nos. 9295, 7225, and 8821, displayed flash points of 45°, 60°, and 72°C, respectively.

The flammability limits apparatus was calibrated with isooctane. A flammability limits diagram for the isooctane vapor/water/air system was determined, and this is presented as Figure 18. The results are in reasonable agreement with literature values (12) for the rich and lean limits of neat isooctane. No literature data on isooctane/air/water vapor could be found. Results of flammability measurements on the diesel fuel vapor/water vapor/air mixtures are presented in Figures 19, 20 and 21. The point of peak flammability, i.e., the water vapor content at which the lean and rich flammability limits converge, occurs in the range of 2 to 2.5 mole percent fuel vapor and 23 to 24 mole percent water vapor, which is similar to that observed for the isooctane calibration fuel.

At the completion of the foregoing experiments, a portion of the apparatus for measuring flammability limits was modified to accommodate the measurement of vapor pressure. The purpose was to determine if water-in-fuel microemulsions are truly immiscible systems. Earlier work conducted elsewhere for the Army Research Office (ARO) (13) indicated that water-in-fuel macroemulsions were immiscible systems, i.e., the vapor pressure of water above the macroemulsion was about the same as that of pure water and did not depend on the concentration of water in the emulsion. However, for the present work, it was recognized that the vapor pressure of water could be concentration dependent in microemulsions.

The apparatus modification comprised replacing one of the heated reservoirs shown in Figure 22 with an aluminum cell designed for precise temperature control (in a thermostated bath) and measurement (Figure 22). The fuel sample in this container is frozen with a dry ice/acetone bath, and it is then pumped down, thawed, and pumped down again, successively, until the residual pressure is well below 10^{-4} atm, thereby removing all noncondens-

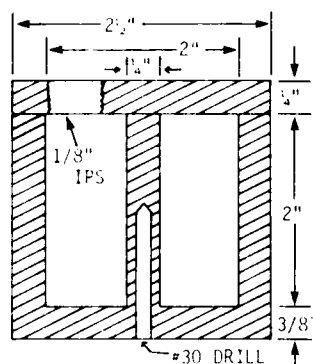
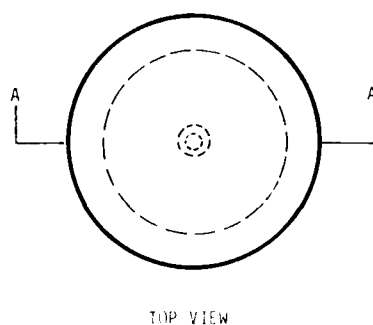


FIGURE 22. DRAWING OF
VAPOR PRESSURE CELL

able gases from the fuel sample. The vapor pressure is then measured directly with the appropriate pressure transducer in the apparatus illustrated in Figure 16 as the deaerated fuel in the aluminum block is allowed to equilibrate at various temperatures, ranging from 1° to 100°C.

Vapor pressure measurements were made at 77°C on neat diesel fuel and five blends containing 6 vol% surfactant and 10, 5, 1, 0.5, and 0 vol% added water, respectively. Measurements made on pure water were consistent with vapor pressure tabulations in the literature and showed that the apparatus could yield accurate data. Off-gassing during experiments with diesel fuel containing 6 vol% surfactant indicated

the presence of dissolved water in the neat surfactant. This was subsequently confirmed by chemical analysis. Temperature control of the system proved to be the most critical factor in achieving repeatability. The results of the measurements made on the various fuel blends are presented in Table 27 and described in the discussion accompanying Figure 24 later in this report.

In order to relate the experimental flammability limits and vapor pressure data to the flammability characteristics of FRF, a series of experiments was conducted in a controlled-temperature, horizontal flame propagation channel (Figure 23). In these experiments, the fuel was preheated to 77°C in a closed vessel, while the channel was equilibrated at 77°C. In each experiment, the channel was fully filled with the test fluid, and the illustrated wick was placed in the liquid 15 cm from one end of the channel. The wick

TABLE 27. VAPOR PRESSURE AND COMPOSITION OF VAPORS IN
EQUILIBRIUM WITH AQUEOUS DIESEL/FUEL MICROEMULSIONS AT 77°C

Microemulsion Composition							Water Content of	
Water Added, vol%	Water from Surfactant, vol% (1)	Water from Base Fuel, vol% (2)	Total Water, vol%	Ratio of Water to Surfactant		Measured Pressure, atm	Fuel/Air/Water Vapor Mixture, Mole % (4)	
				vol/vol	mol/mol(3)			
9.09	0.046	0.007	9.14	1.52	42.1	0.377	0.996	33.5
4.76	0.048	0.007	4.82	0.80	22.2	0.358	0.997	31.6
0.99	0.050	0.007	1.05	0.175	4.9	0.294	0.994	25.2
0.50	0.051	0.007	0.55	0.092	2.6	0.258	0.994	21.6
0.00(5)	0.051	0.007	0.058	0.0097	0.3	0.141	0.993	9.9
0.00(6)	0.000	0.007	0.007	--	--	0.043	0.989	0.0(6)

- (1) Calculated from measured water content of surfactant.
- (2) Calculated from equilibrium solubility of water in kerosine at 25°C (API Data Book).
- (3) Calculated with 474 molecular weight of surfactant.
- (4) Calculated from listed vapor pressure data assuming base fuel partial pressure constant at measured valve.
- (5) Base fuel plus Surfactant (84 vol AL-8821 plus 6 vol EA-99).
- (6) Base fuel (AL-8821)(Nil water vapor pressure at 77°C).

was then lighted at one end, and the time required for the flame to traverse across the wick was noted. Subsequently, the time required for the flame to depart from the wick (induction period) and the additional time required for it to traverse the length of the channel were recorded. Results thus obtained with fuel-plus-surfactant blends containing 10, 5, 1, 0.5, and 0 vol% added water are presented in Table 28 and discussed in conjunction with Figures 24 and 25 in a later section of this report.

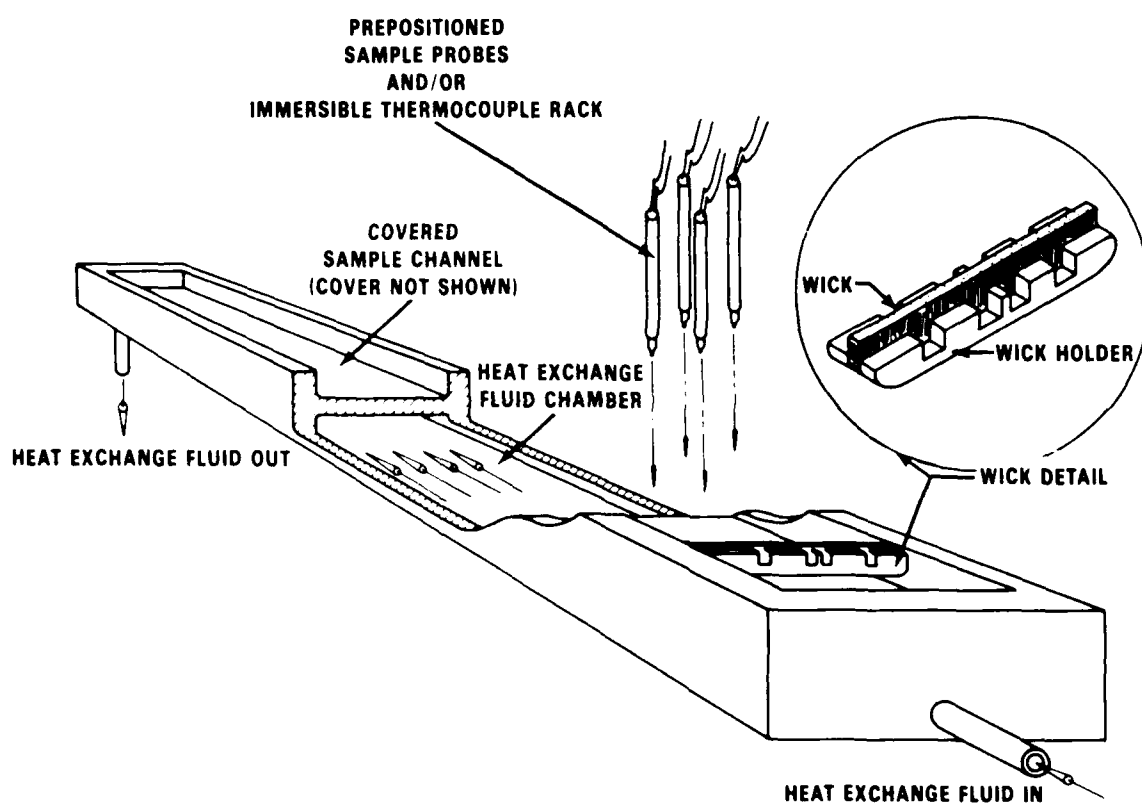


FIGURE 23. ILLUSTRATION OF CONTROLLED TEMPERATURE HORIZONTAL
FLAME PROPAGATION CHANNEL

TABLE 28. SUMMARY OF FLAME CHANNEL POOL BURNING DATA FOR
WATER-CONTAINING, SURFACTANT-STABILIZED, 70°C (158°F) FLASH POINT
DIESEL FUEL AT 77°C (170°F)

	<u>Wick Traverse Time, sec</u>	<u>Induction Period, sec</u>	<u>Channel Traverse Time, sec</u>
Base Fuel (3)*	21 ± 6	63 ± 25 (Undulating Wick Flame)	27 ± 3
93.5 vol% Base Fuel, 0.5 vol% Water, and 6 vol% Surfactant (2)*	15 ± 2	15 ± 6 (Undulating Wick Flame)	36 ± 2
93.0 vol% Base Fuel, 1.0 vol% Water, and 6 vol% Surfactant (2)*	19 ± 5	1200 (Undulating Wick Flame)	No Ignition of Pool
89 vol% Base Fuel, 5 vol% Water, and 6 vol% Surfactant (1)*	30	1200 (Steady Wick Flame)	No Ignition of Pool
84 vol% Base Fuel, 10 vol% Water, and 6 vol% Surfactant FRF (1)*	66	1200 (Steady Wick Flame)	No Ignition of Pool

* Number in parentheses denotes the number of tests.

Flash point anomalies have been observed with various batches of FRF made with the same or with different base fuels. These were re-examined by conducting flash point measurements on a series of 10 vol% water, FRF blends in which the surfactant content was varied from 1 to 13 vol%, in 1-percent steps, using the reference base fuel, No. 8821. Such measurements were also made on 10 vol% water, FRF blends containing 1, 6, and 10 vol% surfactant, using a lower flash point base fuel, No. 7908. Results of these tests are presented in Table 29 together with flash point data previously obtained with these and other base fuels. Table 29 also includes results of mist flammability evaluations.

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RESEARCH ON FIRE-RESISTANT DIESEL FUEL.(U)

SOUTHWEST RESEARCH INST SAN ANTONIO TX ARMY FUELS AN--ETC F/G 21/4
RESEARCH ON FIRE-RESISTANT DIESEL FUEL.(U)

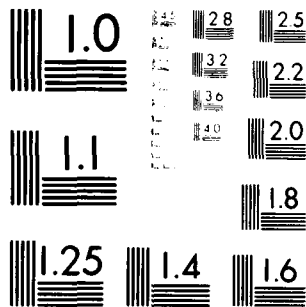
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TABLE 29. FLAMMABILITY OF FRF BLENDS

Code No. of DF-2 Base Fuel	Volume %		Pensky Martens Closed Cup Flash Test (2)(ASTM D 93)				Cleveland Open Cup (ASTM D 92)		AFRL Mist Flashback Rating, cm
	Surfactant(l)	Water	Pilot		Flash Point, °C	Fire Point, °C			
			Blowout, °C	Outside Flash, °C					
6938	0	0	---	---	58	88	---	20	
7225	0	0	---	---	60,61	84	---	22	
	1	1	---	---	64	90	---	---	
	3-5	5	---	---	66,66	94	---	---	
	6	10	---	---	60,61,65, 66,67	100,103	---	17,15	
	6	10	77	82	NF	---	---	---	
	10	10	77	82	NF	---	---	---	
	6	10-16	---	---	---	---	---	---	
7908	0	0	---	---	54,54	---	---	---	
	1	10	77	85	NF	---	---	---	
	6	10	---	---	58,58	---	---	---	
	10	10	77	85	NF	---	---	---	
7907	0	0	---	---	63	---	---	---	
	6	10	---	---	NF	---	---	---	
7996	0	0	---	---	68	---	---	---	
	6	10	---	---	NF	---	---	---	
8821	0	0	---	---	70,72	---	---	---	
	1	10	77	93	NF	---	---	---	
	2	10	77	93	NF	---	---	---	
	3	10	77	93	NF	---	---	---	
	4	10	77	88	NF	---	---	---	
	5	10	77	88	NF	---	---	---	
	6	10	77	88	NF	---	---	---	
	7	10	82	91	NF	---	---	---	
	8	10	82	91	NF	---	---	---	
	9	10	82	91	NF	---	---	---	
	10	10	77,77	93,82	NF	---	---	---	
	11	10	77	82	NF	---	---	---	
	12	10	77,77	84,82	NF	---	---	---	
	13	10	77	82	NF	---	---	---	
8445	0	0	---	---	75	---	---	---	
	6	10	---	---	NF	---	---	---	
7931	0	0	---	---	88	---	---	---	
	6	10	---	---	NF	---	---	---	

(1) Surfactant TAN = 15.5 mg KOH/g

(2) "NF" means no normal flash point could be observed. All values are the average of at least two tests, including those rated "NF."

The flash point data appear to demonstrate ambiguous results. Flash points were observed with FRF blends prepared from base fuels having flash points of about 61°C or less. With FRF blends made from higher flash point base fuels, the pilot flame was extinguished by the vapors escaping from the apparatus. During the course of these tests, blowout of the pilot flame was observed between 77° and 82°C. Upon further increase of temperature, a flash was observed (between 82° and 93°C) outside of the cup, near the external relight flame, as the window of the apparatus was opened. Apparently, a flammable mixture formed as vapors from the previously closed cup escaped into the atmosphere and became diluted with air. When the liquid temperature in the apparatus reached 100°C, vigorous boiling was observed, at which time the tests were terminated. If no normal flash point could be observed, the letters "NF" appear in Table 29. It should be noted that each time "NF" was observed, a duplicate run was performed to substantiate the results. The flammability mitigation mechanism implications of these results are illustrated in Figure 26 and the accompanying discussion in the following section of this report.

Discussion of Observed Inter-relationships Among Vapor Pressure, Flammability Limits, Flash Points, and Pool Flame Propagation

As demonstrated by the data of Figure 24, the equilibrium water vapor partial pressure over FRF liquids containing varying amounts of water exhibits significant concentration dependence and is substantially less than the vapor pressure of pure water. The equilibrium vapor water content data points for 0.058, 0.55, and 1.05 vol% water in the liquid are essentially linear in this semilog plot, and the points for 4.8 and 9.1 vol% water extrapolate essentially linearly in this plot to the value of 41 mole percent water vapor in air for 100 percent liquid water. The transition in slope between these linear regions of the plots suggests a transition in the nature of the liquid phases. It should be noted that if these various blends behaved as true immiscible systems, the 41 percent value for 100 percent liquid water would have been observed in each case; hence, all of these liquids appear to behave as nonideal solutions rather than as immiscible systems.

It is of interest to consider the following implications of the observed vapor composition versus water content measurements:

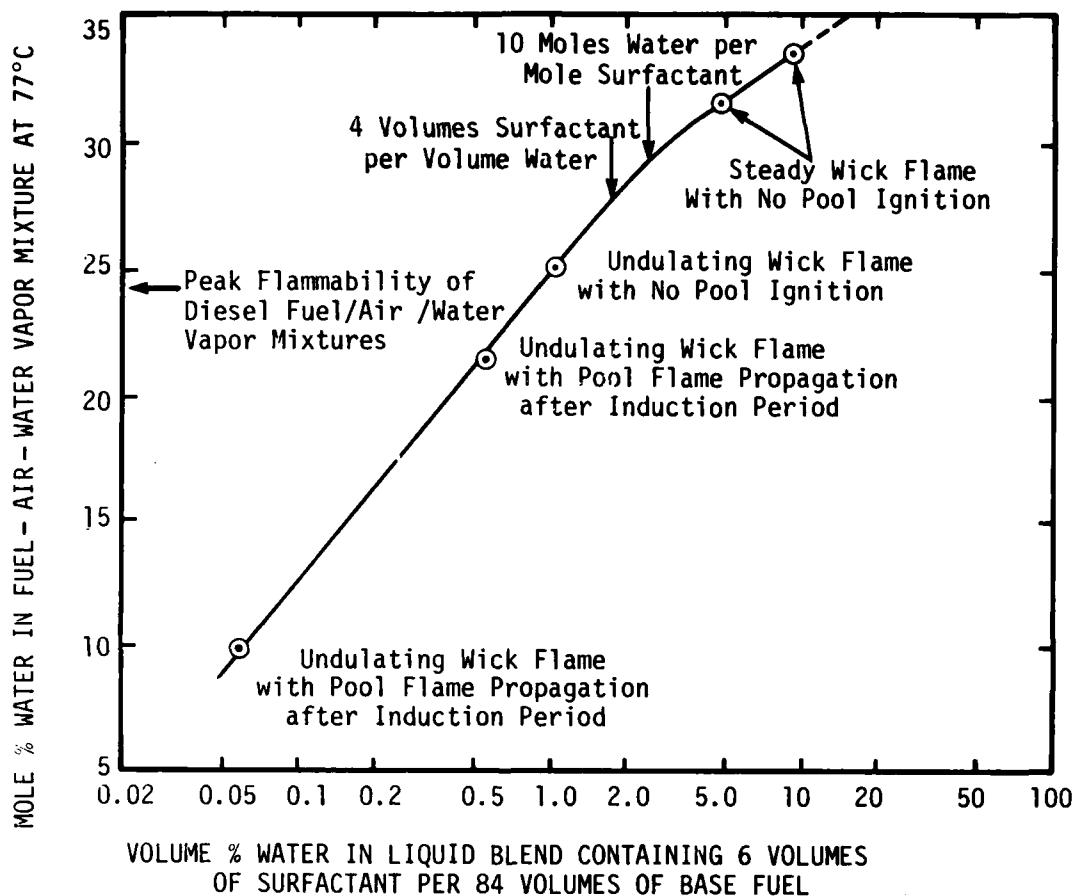


FIGURE 24. EQUILIBRIUM VAPOR COMPOSITION AND FLAMMABILITY CHARACTERISTICS VS FRF WATER CONTENT

- The observed transition in slopes between high water concentrations and low water concentrations is not in disagreement with published observations. It has been predicted theoretically (14) and observed experimentally (10,15) in isooctane/aerosol/OT/water systems that when the volumetric ratio of surfactant to water is more than about 4, the systems behave as micellar solutions. In such solutions, the polar heads of the surfactant molecules are interlinked by hydrogen bonding,

via bound water, forming "swollen" micelles (10). With larger volumes of added water, a discrete water phase is present within each surfactant-surrounded droplet, and the systems behave as either microemulsions or macroemulsions, depending on the amount of water present and other system parameters. With FRF-type systems, the above-mentioned surfactant-water ratio of 4 lies within the slope transition region of Figure 24. Hence, this transition could correspond to a transition between microemulsions and micellar solutions.

- Based on analyses for water in the surfactant by the Karl Fischer method, 18 mole percent water dissolved in the surfactant (0.8 wt%) appears to be responsible for the partial pressure of water of about 0.1 atm at 77°C. This is greater than the maximum predicted by Raoult's law for an ideal solution of water in surfactant (0.04 atm), and such ideal solution behavior would not be expected in this polar system. Some enhancement of water vapor pressure would be expected due to the extremely small droplet size; however, additional excess water vapor partial pressure would not be in disagreement with published observations (10,15). It has been noted that, when the molar ratio of water to surfactant is less than about 10 in isooctane, water becomes much more volatile than the isooctane solvent and "boils" out of the solution at temperatures above 50°C. Even if vapor pressure enhancement caused by droplet surface curvature were accounted for, it has been argued such boiling should not occur below about 90°C (10). This apparent increase in the volatility of water indicates that the bound water released by raising the temperature is different from normal liquid water (10). Whereas normal liquid water contains structures caused by intermolecular hydrogen bonding, this micellar water may be, at least temporarily, less structured or even truly monomolecular. Additional evidence of this difference is provided by the observation (10) that, when a micellar solution of water/surfactant/isooctane is diluted with dry isooctane, water molecules rapidly migrate from the micelle core to re-establish the equilibrium dissolved water content in the isooctane phase. Such equilibration is much slower in the absence of surfactants (10), possibly reflecting the slower diffusion rates of associated groups of water molecules relative to less structured or possibly monomolecular water.

It is well established that the vapor pressure of normal liquid water is much lower than it would be if hydrogen bonding could not occur. Hence, in view of the foregoing published observations and the fact that the above-mentioned water-surfactant molar ratio of 10 also lies within the slope transition region of Figure 24, it is reasonable to consider the possibility that the anomalously high partial pressure of water observed in this laboratory for the water/surfactant phase in diesel fuel micellar solutions may have stemmed, at least in part, from the less associated or possibly monomolecular nature of the bound water released by heating the solutions to 77°C. If such is the case, the observation of excess partial pressure of water implies the existence of an equilibrium between the "bound water" and water vapor. This would differ from the usual equilibrium between normal structured water and water vapor.

Also shown in Figure 24 are the results of pool flame propagation experiments corresponding to each data point. Figure 25 presents a composite of all of the flammability limits data for the 45°, 60°, and 72° C flash point diesel fuels, where the flammable envelope is drawn to include all ignitions. The peak flammability derived from this composite plot is also shown in Figure 24 where it displays quantitative agreement with the indicated pool flame propagation results. FRF blends having equilibrium vapors containing less than 24 percent mole water exhibit pool flame propagation whereas those producing higher water-content vapors do not. In fact, the case where the liquid contains 1 vol% water (25 mole% water in the equilibrium vapor) displayed an undulated wick flame which was almost capable of departing from the wick, whereas the wick flame was steady for FRF blends containing 5 liquid vol% or more water.

The interrelation of the foregoing vapor composition, flammability limits, and flash point data which are shown in Figure 26, provides strong evidence that vapor blanketing is a dominant mechanism in the self extinguishment of FRF pool burning. As noted in the figure, the

solid line represents pure water in immiscible systems. The open circle data point corresponds to 10 vol% water in the liquid blend from Figure 24. The solid data point corresponds to the peak flammability of Figure 25 at the maximum observed flash point in Table 29. Accordingly, the dashed curve in Figure 26 is a tentative estimate of the equilibrium water vapor content above 10 vol% water FRF blends at various liquid temperatures. This estimate is subject to confirmation by additional vapor pressure studies. If it is substantiated, and if subsequent pool flame propagation temperature gradient measurements confirm that the results are applicable to the dynamic nonequilibrium case, vapor blanketing can be labeled the dominant mechanism. However, if the subsequent studies reveal significant evaporative liquid surface cooling or other complexities in the dynamic case, the relative importance of other possible mechanisms will be investigated.

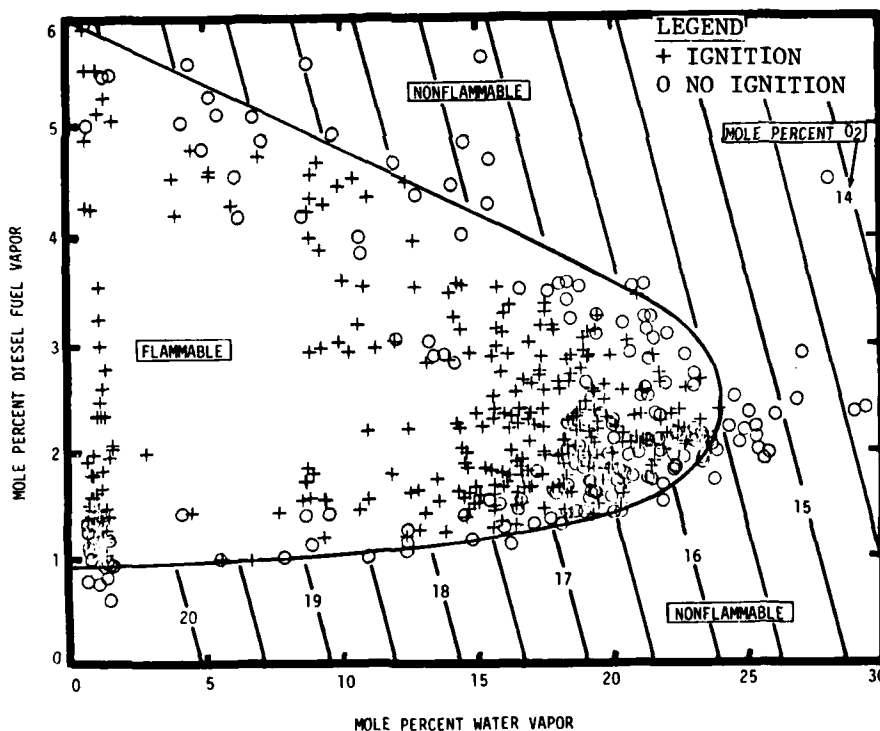


FIGURE 25. COMPOSITE FLAMMABILITY DIAGRAM FOR 45°, 60°, AND 72°C FLASH POINT DIESEL FUELS

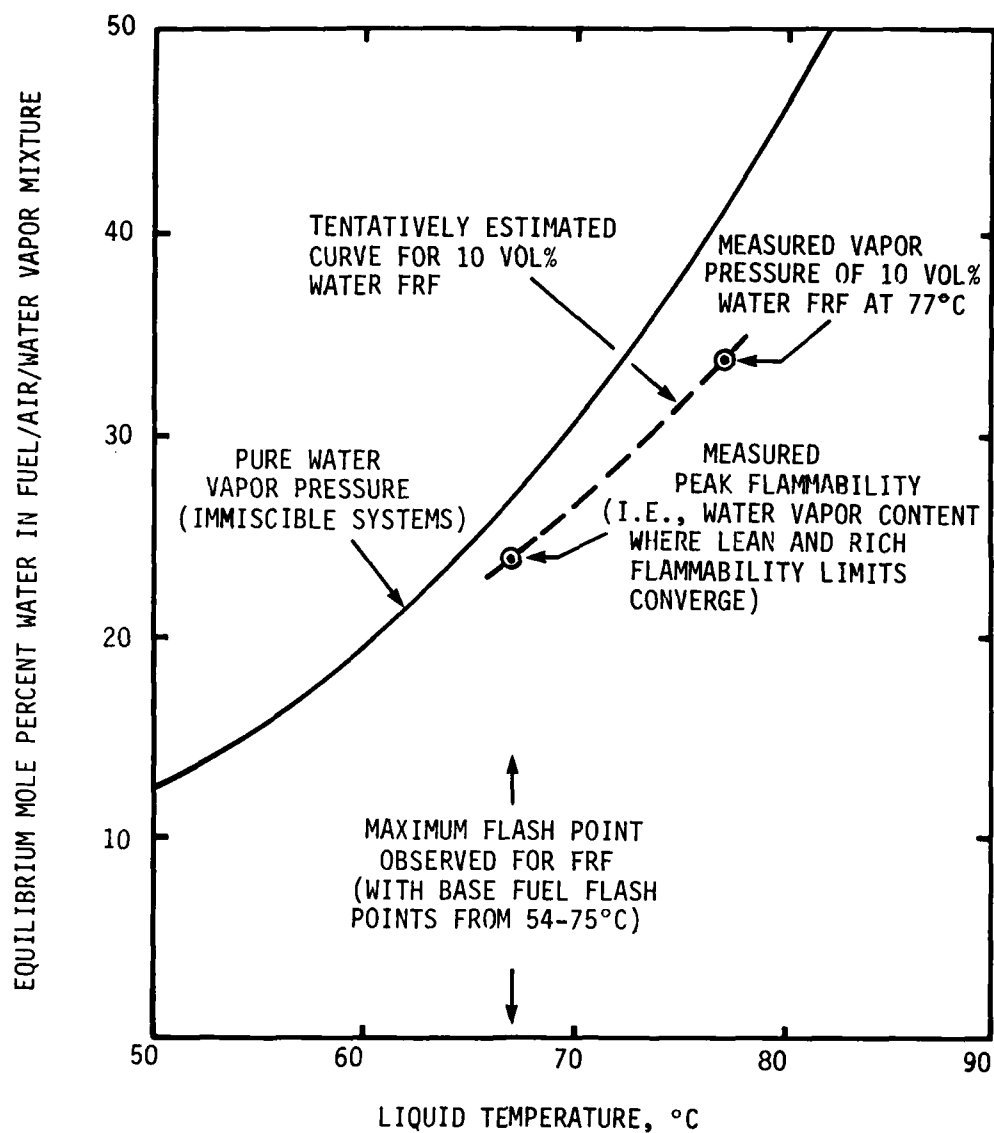


FIGURE 26. CORRELATION OF MAXIMUM FLASH POINT OF FRF WITH PEAK FLAMMABILITY AND VAPOR PHASE COMPOSITION VS LIQUID TEMPERATURE

IV. ADVANCED DEVELOPMENT RESEARCH

A 400-hour NATO cycle endurance test of FRF was initiated at the U.S. Army Tank Automotive Command (TACOM) for MERADCOM using an AVDS-1790-2C diesel engine (M60 battle tank engine). This laboratory provided support for this advanced development research. The research was essentially divided into two separate tasks.

Task 1--FRF Continuous Blending System

A purchase order was issued by this laboratory to a commercial vendor for an in-line blending system of 100 gal./hr (320 kg/hr) of FRF capacity. During shakedown testing of the system prior to shipment, it was determined by AFLRL personnel that the system would not perform satisfactorily. Because of its importance to the AVDS-1790 endurance test and to expedite its satisfactory completion, the system was shipped to AFLRL for modification.

The following actions were taken after the system was delivered to this laboratory:

- Complete disassembly to allow re-enforcement of the (warped) base supporting the blending system.
- Cleaning and adjustment of the proportioning pumps to determine if repeatable metering of fluids could be obtained. Results appeared acceptable.
- Re-assembly of components in stages in order to determine if properly proportioned fluids could be metered simultaneously.
- Documentation of the quantity of fuel components being metered separately was accomplished. Satisfactory repeatability was obtained.
- Installation of a different type of static mixer for blending surfactant with base fuel and for blending water with the surfactant/fuel

mixture. Results indicated that the static mixers not only achieved dissolution of the surfactant in the fuel but also provided adequate mixing to blend the fuel and water in the second stage of the mixing process.

The final mixing system is composed of the following components, which are illustrated in Figure 27.

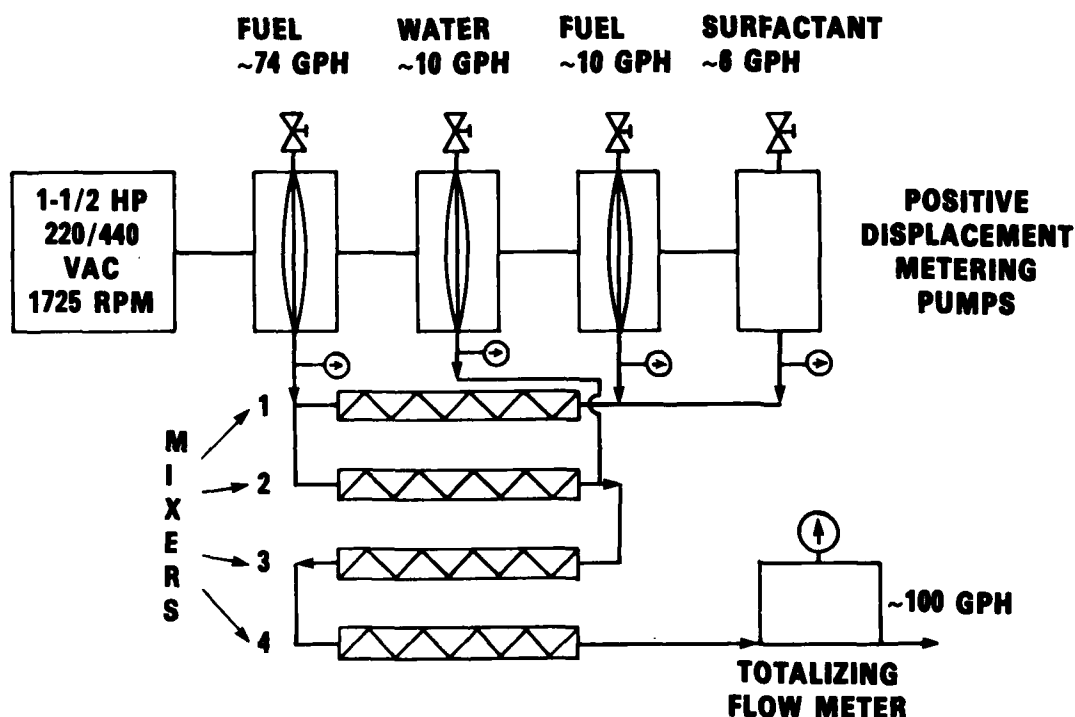


FIGURE 27. SCHEMATIC FLOW DIAGRAM--100 GAL/HR FRF BLENDING SYSTEM

First Stage: The surfactant (6 vol%) is preblended with diesel fuel (approximately 12 vol% of fuel) through a 32-element Kenics® mixer.

Second Stage: This preblend of fuel and surfactant is blended with the remaining fuel (72 vol%) through another 32-element Kenics mixer.

Third Stage: The fuel-surfactant blend is then blended with water (10 vol%) through two 32-element Kenics mixers in series. Results thus far have

shown that this final stage successfully blends the fuel-surfactant-water mix into a stable emulsion similar to the results obtained in the laboratory. The individual component concentration has been documented by actually weighing the amount used to prepare a known volume of fuel blend. The total fuel volume is then measured through a Hersey totalizing meter.

The 100 gal/hr continuous FRF blending system was installed at TACOM with the assistance of AFLRL personnel. Figure 28 is a diagram of the test cell at TACOM, housing both the engine and the FRF blending system. The FRF blending system was designed to provide both fuel and water at constant head pressures by automatically maintaining constant levels in the fluid supply drums with float control valves. The surfactant supply drum is filled on a daily-use basis. The FRF is stored in a 300-gal. storage tank also located in the test cell. A fuel control panel is set up to provide either FRF or neat fuel to the AVDS-1790 engine. After installation and shakedown testing, the blending system was operated continuously, pumping into a 300-gal. reservoir. After approximately 160 gallons of FRF had been prepared, two samples were taken so that water content could be analyzed at AFLRL. The results of these analyses are as follows:

	<u>Analysis 1</u>		<u>Analysis 2</u>	
	<u>wt%</u>	<u>Vol%</u>	<u>wt%</u>	<u>vol%</u>
160-gal Sample 1	11.9	10.4	11.7	10.3
160-gal Sample 2	11.8	10.3	11.6	10.2
150-Hr sample	11.3	10.0	11.1	9.9

After 150 hours of engine endurance testing, a sample was taken, and the analysis of this sample (in table above) confirms that the water content is still nominally 10 vol%. Incidentally, this sample is still a stable translucent microemulsion after standing in this laboratory for over 6 months.

The blending system has been operated many times, originally in this laboratory and subsequently at TACOM, and has never failed to produce a stable microemulsion, provided the components are in (or near) the proper ratio. An abbreviated operating manual for this modified system is presented in Appendix A.

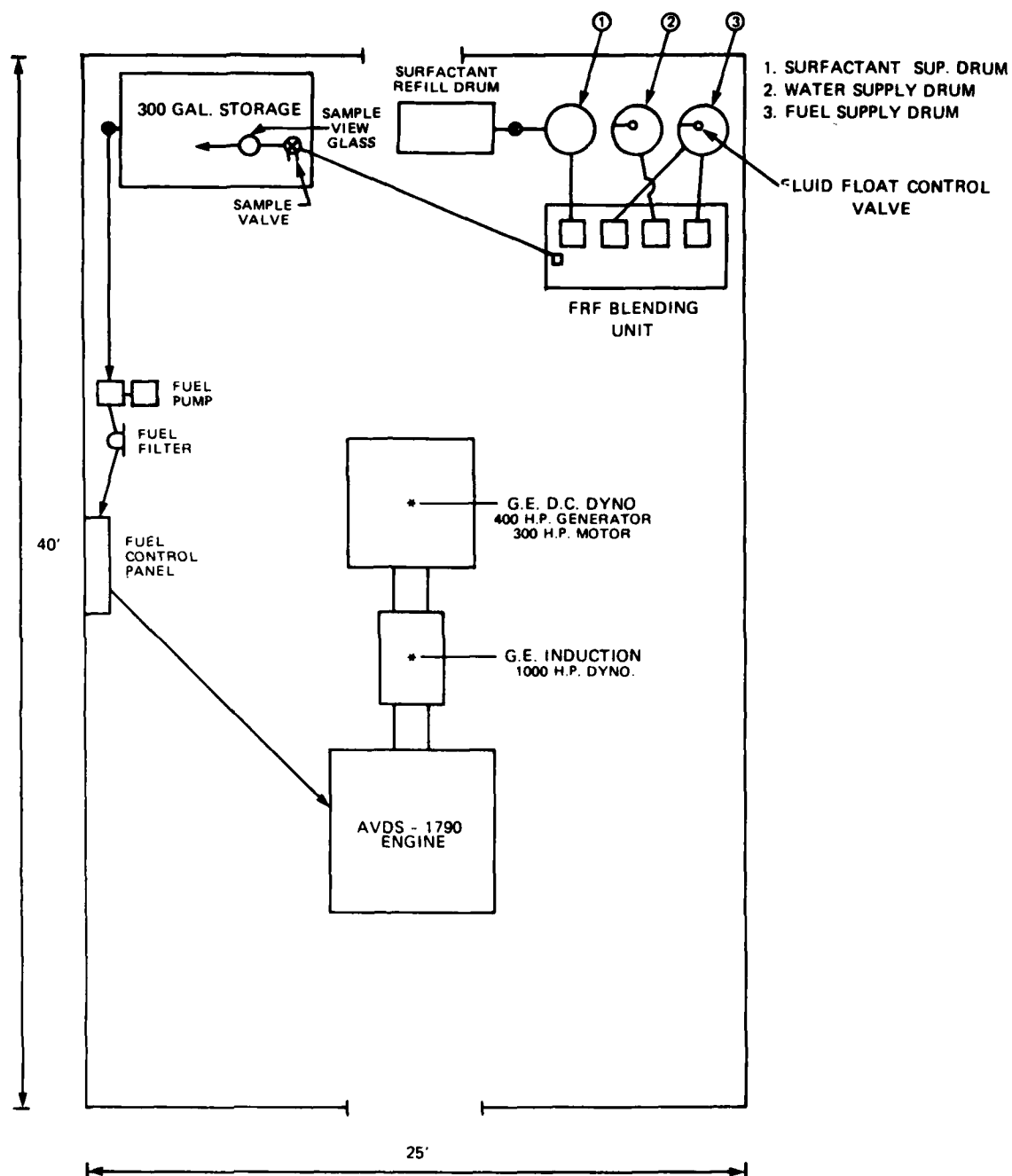


FIGURE 28. DIAGRAM OF ENGINE TEST CELL AT TACOM USED FOR AVDS-1790-2C FRF TEST

Task 2--AVDS 1790-2C 400-Hour NATO Cycle FRF Endurance Test

Personnel from this laboratory met with TACOM personnel during the planning stages of this project, and later during the engine test. The details of the test program developed by TACOM are presented in Appendix B. TACOM provided this laboratory with a sample of the base fuel obtained in bulk for this test. Its analysis is presented in Table 30. It was determined that stable microemulsions could be prepared repeatably with this fuel using surfactant with a TAN of 17 to 19 mg KOH/g and water containing 0 to 300 ppm TDS. MERADCOM personnel purchased sufficient emulsifying agent for the TACOM 400-hour test. Its TAN of 19 mg KOH/g proved satisfactory with TACOM (Warren, MI) tap water.

An Anniston Army Depot-rebuilt AVDS 1790-2C was installed in a test cell at TACOM as illustrated schematically in Figure 28. The test program was initiated after satisfactory initial shakedown testing. Initial estimations of fuel consumption by TACOM personnel indicated that approximately 12,000 gallons of FRF fuel blend would be consumed during the 400-hour endurance test period and additional hours spent in power and performance checks.

A nonfuel-related mechanical problem developed at 10 hours into the 400-hr endurance test cycle. One cylinder had developed a crack which forced a stoppage of the endurance test. This cylinder assembly was successfully replaced and, after baseline checks with neat fuel, the endurance test was resumed. Further delays were encountered due to dynamometer loading problems; however, these were quickly alleviated, resulting in only several days of delay. Samples of the new and used (10-hour) lubricant were analyzed at AFLRL to determine if changes had occurred in the lubricant during this short test interval. The results presented in Table 31 show that essentially no differences were detectable. It had been reported that the oil had been changed just prior to initiating the endurance test of FRF.

Exhaust emission samples were collected by personnel from Edgewood Arsenal while the engine test continued. These samples were returned to Edgewood Arsenal where analyses were to be made for the following compounds: die-

TABLE 30. ANALYSIS OF TACOM VV-F-800C-DF-2 DIESEL FUEL
(AFLRL NO. 10135F)

Property	ASTM	Specification Value	Actual Value
Gravity, API at 15.5°C	D 287	---	34.2
Density, g/ml at 15.5°C	D ---	---	0.8535
Flash Point, PMCC, °C	D 93	---	61
Flash Point, COC, °C	D 92	---	91
Fire Point, COC, °C	D 92	---	95
Cloud Point, °C	D 2500	---	-16
Pour Point, °C	D 97	---	-36
Kin Vis, cSt at 40°C	D 445	1.9-4.1	2.39
Kin Vis, cSt at 0°C	D 445	---	6.38
Accel. Stability, mg/100 ml	D 2274	1.5	2.86
Steam Jet Gum, mg/100 ml	D 381	---	6.7
Copper Strip Corrosion	D 130	3	1a
Total Acid Number, mg KOH/g	D 664	---	0.64
Water Content, wt%	D 1744	0.01	0.02
Sulfur by XRF, wt%	---	0.5	0.35
Carbon, wt%	---	---	86.91
Hydrogen, wt%	---	---	12.64
Aromatics by HPLC, wt%	---	---	33.4
Aromatic Ring Carbon by UV, wt%			
mononuclear			9.7
dinuclear			10.6
trinuclear			0.6
total			20.9
Heat of Combustion, Gross, Btu/lb	D 240	---	19,485
Heat of Combustion, Gross, MJ/kg	D 240	---	45.32
Heat of Combustion, Net, Btu/lb	D 240	---	18,330
Heat of Combustion, Net, MJ/kg	D 240	---	42.64
Cetane Number	D 613	45	43
Distillation	D 86		
% Evaporated, °C			
IBP		---	186
5		---	210
10		---	220
15		---	228
20		---	233
30		---	241
40		---	258
60		---	267
70		---	276
80		---	287
90		338 max	302
95		---	320
EP		371 max	338
Recovered, %		---	98.5
Residue, %		---	1.5

TABLE 31. NEW AND USED OIL ANALYSIS FROM TACOM AVDS-1790-2C ENGINE TEST OF FRF

<u>Test</u>	<u>New Oil</u>	<u>Used Oil (10 Hr)</u>
TAN	2.29	2.18
TBN	13.00	12.86
Fuel Dilution (GC)	0.1%	0.2%
K.F. Water Content	0.2%	0.2%
Elemental Analysis		
Ca, %	0.50	0.51
Zn, %	0.09	0.09
P, %	0.07	0.07
S, %	0.62	0.62
Fe, ppm	7	10
Cr, ppm	---	---
Cu, ppm	4	5
Pb, ppm	9	11
Viscosity, cSt at 40°C	105.9	107.9
Viscosity, cSt at 100°C	11.6	11.7
Viscosity Index	96	96

thanol amines, nitrosoamines, cyanides and aldehydes. No results have yet been received.

After 168 hours of operation, a major nonfuel-related failure occurred in the AVDS-1790 engine. It was reported by TACOM personnel that cylinders 3 and 4, left side, had intake valve problems. Further inspection revealed a valve break at a weld joint between the stem and tulip with subsequent massive piston/cylinder failure. It has been reported that similar valve separation is not uncommon and causes valve train misalignment, resulting in valve damage in adjacent cylinders. Based on the results of the damage inspection, it was concluded that the test should be terminated. Disassembly and inspection of the AVDS-1790 engine were conducted. An experienced AFLRL engine rater inspected the cylinder parts from the undamaged side. This inspection did not reveal any abnormal fuel-related distress. Meanwhile, TACOM personnel conducted a total teardown to further assess damage caused by the mechanical failure, and a final test report will be issued by TACOM.

V. CONCLUSIONS AND RECOMMENDATIONS

Based on the foregoing data and discussions and previously reported information (1) the following conclusions may be made:

- Fire-resistant diesel fuel (FRF) enhances survivability of personnel and equipment in combat scenarios.
 - Smaller fireball effects result from ballistic penetration.
 - Ground fires/pool fires are self-extinguishing at fuel temperatures well above base fuel flash point, thus providing protection for personnel, vehicles, and storage facilities.
- Fire-resistant diesel fuel microemulsions comprising 10 vol% water, 6 vol% amide/amine/soap emulsifier (EA), and 6 vol% aromatic concentrate (AC) exhibit the following characteristics:
 - Form spontaneously with simple agitation.
 - Form at blending temperatures between 0° and 50°C
 - Are stable for more than a month at 4° to 40°C.
 - Are stable for more than 6 months at 4° to 24°C and in sheltered outdoor exposure.
 - Remain stable through at least six temperature cycles between 2° and 50°C.
 - Are stable with up to 11 to 12 vol% water.
 - Are not adversely affected by dilution with various diesel or JP-5 base fuels.
 - Are compatible with conventional diesel fuel additives.
 - Are compatible with normal contamination levels of dirt.
 - Provide corrosion protection to steel surfaces.
 - Can be inhibited with aryltriazoles to mitigate corrosion of copper and its alloys.
- The preferred compositions of base fuel, water, emulsifier, and aromatic concentrate for producing satisfactory FRF microemulsions are as follows:
 - Base fuel composition window: total aromatic ring carbon (TARC) in 78 vol parts base fuel plus 6 vol parts aromatic concentrate (AC) between 15 and 20 wt%.
 - Water composition window: potable water with total dissolved

- solids (TDS) content of 50 ppm or less.
- Emulsifier composition: Kritchevsky amide (EA), made from two moles of diethanolamine (DEA) per mole of oleic acid, adjusted with oleic acid to total acid number (TAN) of 15.5 mg KOH/g.
- Aromatic concentrate composition: 99+ wt% colorless C_9+ aromatic hydrocarbons.
- Other compositions with satisfactory phase stability have been identified, and the influence of fuel TARC, water TDS, and emulsifier TAN have been documented.
- The quality of FRF microemulsions may be expressed in terms of appearance, phase, stability, composition, and physical properties:
 - The visual appearance of stable FRF microemulsions can be quantitatively related to the optical absorbance in the wavelength range of 500 to 600 nm.
 - The translucent microemulsions' average hydrodynamic diameter (rigid spherical droplets) are less than 300 Å (0.3 nm) by photon correlation spectroscopy (quasi-elastic light scattering).
 - FRF water content can be measured quantitatively with the Karl Fischer method or by heat of adsorption technique not yet fully developed for this use. Other promising, but not developed, water analysis methods for FRF include microwave absorption, or calorimetry, and dielectric constant measurement.
- Diesel engines will start, run, and idle satisfactorily on FRF
 - Volumetric net heat of combustion is 11 percent lower with FRF
 - Rated power is decreased with FRF at original maximum rack setting
 - Rated power is recoverable with some engines by adjustment of maximum rack setting
- Flow properties, particularly at low temperatures, represent a yet-to-be-resolved problem area.
 - Some FRF blends exhibit unsatisfactorily high and time-dependent viscosities at 20°C or lower temperatures.
 - The use of such additives or anti-icing agents does not prevent cavitation resulting from filter plugging on the suction side of a fuel pump at filter temperatures below 0°C.
- Advanced development research provided useful information on FRF systems and utilization.

- FRF is repeatably produced successfully in a 100-gal./hr continuous blending system.
- The AVDS-1790-2C M60 battle tank engine experienced no fuel-related mechanical or performance degradation during a NATO-cycle endurance test. The test was terminated after 168 operating hours due to mechanical failure of an intake valve.
- Basic research on the mechanisms of FRF flammability mitigation has documented effects of water vapor on flammability limits and identified several unique characteristics of fuel/surfactant/water systems.
 - The lean and rich flammability limits of typical diesel fuel vapors converge when the water content of the fuel/air mixture is increased to about 24 mole %.
 - When the equilibrium water vapor concentration above FRF at the flash point of its base fuel exceeds about 24 mole %, no flash point is observed; conversely, when it is less than about 24 mole %, a flash point about equivalent to that of its base fuel is observed.
 - When the water content of the liquid at 77°C is less than 1 liquid vol%, the equilibrium water vapor content above the liquid is less than about 24 mole %.
 - Pool flame propagation occurs only when the liquid phase water content is less than about 1 liquid vol%.
 - Water vapor partial pressures are strongly dependent on the water content of the equilibrium liquid.
 - An apparent transition in phase behavior is observed as the liquid phase water content is increased from less than 1 liquid vol% to greater than 5 liquid vol%, suggesting a transition from micellar solutions to microemulsions.

The foregoing conclusions reveal the most significant problem area to be that of unsatisfactory low-temperature flow properties and filtration characteristics with some base fuels. Because of this and other considerations, it is recommended that continuing studies be devoted to the following tasks.

- Define Utilization Envelope for FRF
 - Low-temperature properties

- Marginal ignition quality
- Engine Low-temperature operability
- Filterability/pumpability (Low Temp. Limit)
- Additive Effects (Flow improver, etc.)
- Other surfactants
- Flammability Properties
 - Water content requirement at lower test temperatures
 - Screening tests
 - Confirmatory ballistic tests
 - Utilization Properties
 - Cetane number improver response
 - Full-scale vehicular power plant responsiveness and range
 - Effects of FRF carryover on fuel handling systems and other fuels such as JP-4
- Recommend Quality Assurance Methodology
 - Continuous monitoring of blending efficacy
 - Evaluation of FRF in storage or in transit
- Assess Types and Arrangements of Filters in Fuel Systems of U.S. Army Vehicles

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APPENDIX A

OPERATING MANUAL FOR
100 GAL./HR PROTOTYPE
FRF BLENDING SYSTEM

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OPERATING MANUAL

100 Gallons-per-Hour Prototype Blending System For Fire-Resistant Diesel Fuel

GENERAL INFORMATION:

Fire-resistant diesel fuel without added aromatic concentrate (FRF) consists of three components: diesel fuel (84 vol%), surfactant (6 vol%), and water (10 vol%). In the mixing unit, these components are metered and blended in the sequence shown in the schematic flow diagram (Figure A-1). To prepare 100 gallons of FRF per hour, the following blending sequence is maintained.

1. The surfactant at (6 Gal./Hr flow rate) is preblended with a small amount of diesel fuel (at 10 Gal./Hr flow rate). The mixing takes place in the Kenics mixer No. 1.*
2. The preblend is further mixed with the remainder of the diesel fuel (74 Gal./Hr) in Kenics mixer No. 2* to give a uniform solution of surfactant in the diesel fuel.
3. Water (10 Gal./Hr) is mixed with the diesel fuel/surfactant solution through two Kenics mixers (Nos. 3 and 4)* in series to give FRF.
4. The effluent FRF is metered through a positive displacement totalizing flowmeter to a storage tank. Properly blended FRF is a microemulsion and is translucent or transparent. Figure A-2 illustrates a series of emulsions, ranging from "macro" to "micro." Each of these blends contain 10 vol% of water. The number on the label gives the volume percent of surfactant in the bottle. (The remainder of the composition is diesel fuel.) Since the FRF prepared in this mixing unit should contain 6 vol% of surfactant, the blend's appearance should resemble that of bottle No. 6.

*All Kenics mixers are nominally 25 in. long x 0.5 in. O.D. and contain 32 mixing elements.

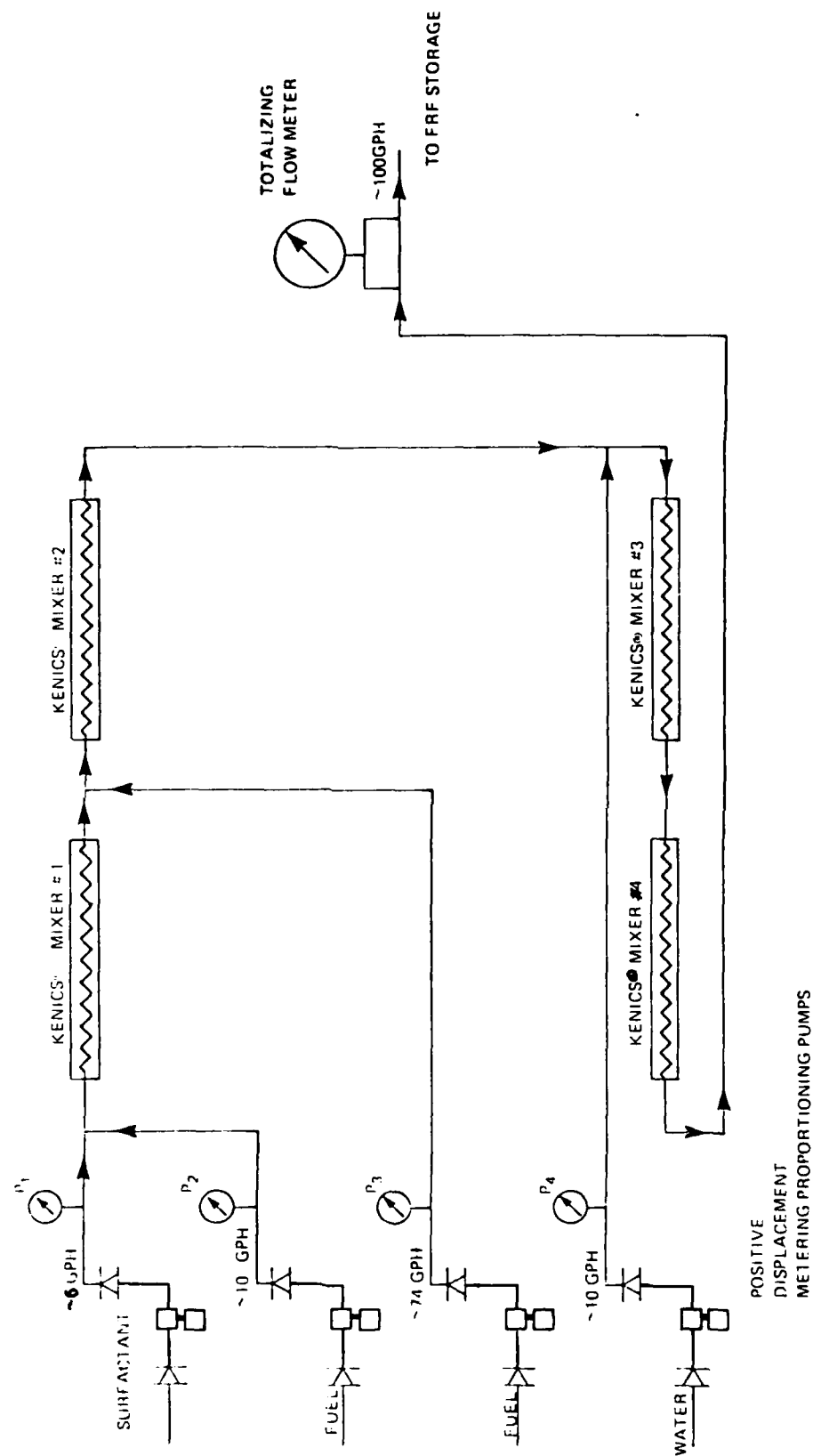


FIGURE A-1. SCHEMATIC FLOW CHART: 100 GAL./HR CONTINUOUS FRF BLENDING SYSTEM

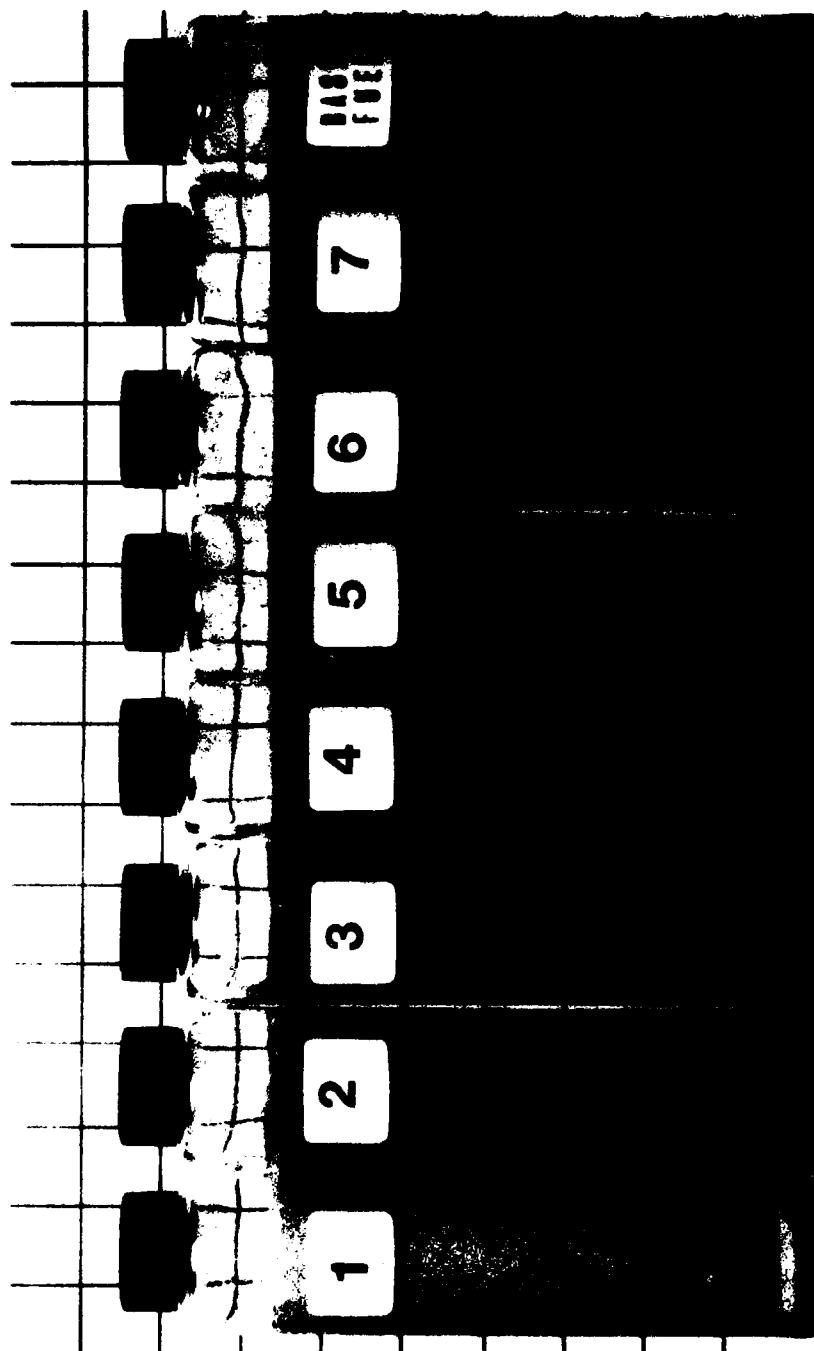


FIGURE A-2. PHOTOGRAPH OF A SERIES OF DIESEL FUEL SAMPLES CONTAINING 10 VOL% WATER (SAMPLES 1-7) AND THE INDICATED QUANTITY OF SURFACTANT (1-7 VOL%).
Neat Base Fuel Is Included for Comparison

OPERATION:

Accurate proportioning of each component is obtained by the use of four Milton Roy positive displacement metering pumps. The surfactant pump head is a plunger type (10.1 Gal./Hr maximum capacity), and all other pumps are disc diaphragm type using hydraulic oil as a working fluid. The maximum capacities of pumps are:

Preblend diesel fuel pump	10.9 Gal/Hr
Water pump	10.9 Gal/Hr
Diesel fuel pump	91.0 Gal/Hr

All pumps are driven by a single 1.5 HP 3-60-230V, 1725 RPM motor. The capacity of each pump is individually preset by a stroke adjustment micrometer. These preset adjustments were made for proper proportioning capacity under normal operating conditions of suction and discharge pressure, and it is important to note that changes in the metering capacity of the pumps are reflected as changes in either the suction or discharge pressures.

Before starting the unit, make sure that:

1. The liquid levels in the water, diesel, fuel, and surfactant supply tanks are at the recommended levels.
2. There is no change in the discharge or inlet plumbing, such as kinks in the supply or discharge hoses, or changes in the sizes or lengths of these hoses (Or equivalent changes due to fittings).
3. The valves between the supply tanks and the pump inlets are open.

Reset the digital flowmeter to zero. Start the system by activating the electric motor. Observe maximum discharge pressure of each pump on the pressure gauges.

The maximum and minimum pressure should be:

Diesel fuel (high flow)	0/90 \pm 5 psig
Water	0/90 psig
Diesel fuel (Low flow)	0/70 psig
Surfactant	0/70 psig

In case the maximum pressures begin to increase above those of normal operating experience (10 psi), shut off the unit immediately. Low pressures or unstabilized pressure readings may indicate that air is still in the system.

A step-by-step operating procedure must be established when this FRF blending system is placed into operation, the specifics of which must be based on the actual installation.

APPENDIX B

TEST PROGRAM FOR AVDS-1790-2C DIESEL ENGINE ENDURANCE

TEST WITH FRF

(Program procedures retyped at AFLRL to provide
master suitable for reproduction.)

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U.S. ARMY TANK AUTOMOTIVE COMMAND
PROPULSION SYSTEMS DIVISION

Test Program AVDS 1790-2C Engine
(Cell 1)

11 June 1980

TITLE: AVDS-1790-2C Engine Test on Fire-Resistant Fuel

PURPOSE:

To determine engine capability to operate on fire-resistant fuel.

OUTLINE OF TESTS:

1. Prepare engine for performance and endurance tests.
2. Install instrumentation.
3. Calibration of instrumentation and equipment.
4. Engine operating limits, adjustments.
5. Engine instrumentation and full load operational check-out.
6. Full load performance (VVF-800 DF-2 Diesel Fuel).
7. Full load performance (Fire Resistant Fuel).
8. 400-hour NATO endurance test (Fire-Resistant Fuel).
9. Disassembly and visual inspection of engine to be conducted after test (conducted in-house).
10. Evaluation of test results and write report.

TEST MATERIAL:

1. Engine Model AVDS 1790-2C.

Type	V
Number of cylinders	12
Method of operation	4 cycle compression ignition, turbocharged air cooled
2. Lubricating oil - Referee, grade 30, conforming to military specification MIL-L-2104C.
3. Fuel - Federal specification VV-F-800C, Diesel grade DF-2.
4. Fuel - Fire-Resistant (FRF).

TEST EQUIPMENT:

Test Cell No. 1, 1400-HP dynamometer, controls associated instrumentation and equipment, Bldg. 212.

TEST PROCEDURES:

1. Prepare engine for performance tests.
 - a. Install engine in test cell and make connections to dynamometer. Make necessary fuel, exhaust and intake air connections. Install cooling tower and fuel throttle and shut-down connections.
 - b. Install all required thermocouples, pressure lines, speed, and load cell connections. Install warning/shutdown bulbs for critical temperature/pressure limits on engine and dynamometer equipment.
2. Instrumentation - Install instrumentation to obtain and record data at each specified speed.

a. Temperature

<u>Item</u>	<u>Range, °F</u>	<u>Accuracy, deg</u>
(1) Air, Cell Ambient (1&R)	60-120	±2
(2) Air, Turbo Inlet (2)	60-120	±2
(3) Air, Turbo Outlet (2)	120-500	±2
(4) Air Inlet Manifold (2)	120-500	±2
(5) Air Cleaner Inlet (2)	60-120	±2
(6) Air Cleaner Outlet (2)	60-120	±2
(7) Exhaust, Before Turbo (2)	200-1500	±10
(8) Exhaust, After Turbo (2)	200-1500	±10
(9) Exhaust, Ports (12)	200-1500	±10
(10) Oil Sump	60-300	±2
(11) Fuel, at Injection Pump	60-120	±2
(12) Fuel, Spill	60-120	±2
(13) Oil, Cooler Outlet	120-300	±2
(14) Engine Oil Gallery	60-300	±2
(15) Instrumentation Bath	60-205	±0.1

b. Pressures, Gauge

<u>Item</u>	<u>Range, °F</u>	<u>Accuracy, deg</u>
(1) Air, Test Cell (In. H ₂ O)	0 to -1	±0.1
(2) Air, Crankcase, Normal (In. H ₂ O)	0 to +15	±1
(3) Air, Crankcase, Blowby (In. H ₂ O)	0 to +15	±1
(4) Air, Engine/Inlet (In. H ₂ O) (2)	0 to -30	±1
(5) Air, Before Cleaner (In. H ₂ O) (2)	0 to -30	±1
(6) Exhaust, Manifold (In. HG) (2)	0 to +50	±1

	<u>Range, °F</u>	<u>Accuracy, deg</u>
(7) Exhaust Outlet (In. H ₂ O) (2)	0 to +50	±1
(8) Fuel Supply (before injection pump) (PSIG)	0 to 10	±0.5
(9) Air, Intake Manifold (In. HG) (2)	0 to 50	±1
(10) Engine Oil Gallery (Manifold) (PSI)	0 to +100	±2

c. Miscellaneous

	<u>Range, °F</u>	<u>Accuracy, deg</u>
(1) Engine Speed (RPM)	0 to 2640 max	±5
(2) Dynamometer Load, (ft-lb)	0 to 1700	±1
(3) Fuel Flow (lb/hr)	0 to 350	±0.1
(4) Crankcase, Blowby (CFM)	0 to 10	±0.1

d. Special Instrumentation Considerations

- (1) Dymec data acquisition system to be used for data gathering.
- (2) Load cell to be used for measuring torque.
- (3) Digital Cox fuel weigh system to be used for measuring fuel.
- (4) Smoke density, Bosch System.
- (5) Temperature reference bath (maintain at 200°F).

3. Calibration of instrumentation and equipment.

All instrumentation and equipment will be calibrated prior to start of test and at ranges specified in the previous paragraph 2.

4. Engine operating limits and adjustments.

a. Observe the following engine operating limits and test conditions for performance and endurance tests.

- (1) Oil to bearing temperature, 240°F warning, 250°F manual return to idle.
- (2) Oil pressure idle, 15 PSI warning, 10 PSI shutdown; maximum oil pressure 70 PSI.
- (3) Air cell Ambient 75° - 85°.
- (4) Fuel temperature at injection pump, 85° ± 5°F.
- (5) Exhaust outlet pressure at full power through speed range 14 to 20 in. H₂O; at idle and part load operation 0 to 14 in. H₂O.
- (6) Nominal fuel flow - 350 lb/hr at 2400 RPM.
- (7) Air pressure turbo inlet (0 to -10 in. H₂O).
- (8) Exhaust temp outlet 1250°F maximum.
- (9) Governed Speeds:
 - a. Idle speed, 675 to 725 RPM
 - b. Maximum speed (No load) 2640 RPM
 - c. Speed (Full load) 2400 to 2450 RPM

5. Engine Instrumentation and Full Load Operational Check-out.

- a. Engine will be run to check leaks, instrumentation, recording and printout systems. The following temperatures and pressures will be maintained.

- (1) Ambient air 75° - 85°F
- (2) Inlet air 75° - 85°F
- (3) Air pressure at turbo charger inlet 0 to -10 in. H₂O
- (4) Exhaust pressure at turbo outlet at full load 14 to 20 in. H₂O
- (5) Fuel at injection pump 85° ±5°F

b. Full load operational check will be made with VV-F-800 diesel fuel, grade DF-2, and will be conducted according to the following schedule. During break-in, continually monitor and observe engine. Do not continue tests if allowed engine operating limits are exceeded. Take complete data and record on log sheet for each break-in period.

<u>Period No.</u>	<u>Time, Min.</u>	<u>Engine, RPM</u>	<u>Observed BHP</u>	<u>Torque (obs)</u>
1	30	700	0	0
2	25	1000	50	262
3	25	1200	70	306
4	25	1400	100	375
5	25	1600	150	492
6	25	1800	300	875
7	20	2000	400	1050
8	20	2200	500	1313
9	15	2400	Full Rack	Record
10	15	1600	150	492
11	15	700	0	0

6. Performance Test (obs net 642 BHP) on diesel fuel VV-F-800, DF-2.

Conduct performance tests with full rack, under the conditions listed in paragraph 4. Record all data listed under instrumentation for engine speeds of 1000, 1200, 1400, 1600, 1800, 2000, 2200, 2400 RPM, up only. At each setting, the engine should be run for a sufficient time for stabilization. Smoke density samples will be taken at each speed setting.

7. Performance Test (Gross 750; Net 642 BHP) on Fire-Resistant Fuel (FRF).

- a. Switch engine to Fire-Resistant Fuel. Operate engine at moderate load to eliminate DF-2 from engine system. (FRF fuel will be supplied through FRF mixing machine. Follow instructions provided with mixer.
- b. Conduct performance tests with full rack, under the conditions listed in paragraph 4. Record all data listed under instrumentation for engine speeds of 1000, 1200, 1400, 1600, 1800, 2000, 2200, and 2400 RPM, up only. At each setting, the engine should be run for a sufficient time for stabilization. Smoke density samples will be taken at each speed setting.

8. 400-Hour NATO Endurance Test on Fire-Resistant Fuel.

- a. The 400-hour NATO endurance will be divided into four periods of 100 hours each. Each 100-hour period is to consist of twenty 5-hour periods as shown in Test Schedule A.

TEST SCHEDULE A

<u>Period</u>	<u>Percent Rated Speed</u>	<u>Percent Load</u>	<u>Time, Hours</u>
1	Idle	0	$\frac{1}{2}$
2	Max Torque	100	1
3	100	0	$\frac{1}{2}$
4	75	85	1
5	100	50	$\frac{1}{2}$
6	100	100	1
7	50	25	$\frac{1}{2}$
TOTAL DURATION			5

Conduct 400-hour NATO endurance test according to Test Schedule A. Values of speeds and torques to be provided by test engineer following completion of performance test.

- b. During 400-hour endurance, the following pressures and temperatures will be regulated to the values as indicated.

(1) Pressures

- a. Air pressure at inlet, 0 to -10 in. H_2O .
- b. Exhaust outlet pressure at full power through speed range, 14-20 inches H_2O : at idle and part load, 0-14 inches of H_2O .

(2) Temperatures

- a. Ambient air 70°-100°F
- b. Inlet air 70°-100°F
- c. Fuel at injection pump 85° ± 5°F
- c. Take 8-ounce oil sample before starting endurance and every 25 hours thereafter, take 2-ounce oil samples. (Purge oil sample line and take sample from oil gallery with engine idling.)
- d. Check engine oil at completion of every 5-hour test period or before engine is started for a new day of test (whichever occurs first).
- e. Data will be recorded during the last 5 minutes of each of the seven periods listed in Test Schedule A, and just before stopping engine.
- f. The following maintenance and adjustments to engine will be conducted after each 100 hour test period, and before power check.

- (1) Change oil.

- (2) Replace oil and fuel filters.
 - (3) Record oil added (less sample) to bring to required level.
 - (4) Visually inspect engine for leaks, breaks, etc.
- g. The 100-hour power check tests shall be conducted under temperature and pressure conditions listed. Record all data listed under "Instrumentation" for engine speeds 1000, 1200, 1400, 1600, 1800, 2000, 2200 and 2400 RPM, up only, and at idle speed. At each setting, the engine should be run for a sufficient time for stabilization. In addition, smoke density samples will be taken at each speed setting.
9. Upon completion of endurance test, obtain photographs of the engine test set-up (photographs can be taken sooner if convenient).
10. Disassemble and conduct visual inspection of the engine at completion of endurance testing, dimensional inspection if required, evaluate results and prepare report.

JOB ASSIGNMENTS:

- 1. DRDTA-TT will be responsible for gathering data, maintaining a daily log book, and test data log, directing personnel and general execution of test.
- 2. DRDTA-RGE will be responsible for day-to-day technical decisions, monitoring test, evaluation of data, and preparing a report.
- 3. Any changes in the above test program shall be mutually agreed upon by DRDTA-TT and DRDTA-RGE and confirmed by a supplement to this basic test program. Each supplement will be evaluated for potential cost and for schedule revisions.

Written By:

Reviewed By:

ROY J.G. RIMPELA
Project Test Engineer

EDWARD J. RAMBIE
Supvr, Mechanical Engineer
DRDTA-RGE

Approved By:

PAUL C. GLANCE
C, Engine Function
DRDTA-RGE

(NOTE: Signatures on original test procedure prepared by TACOM)

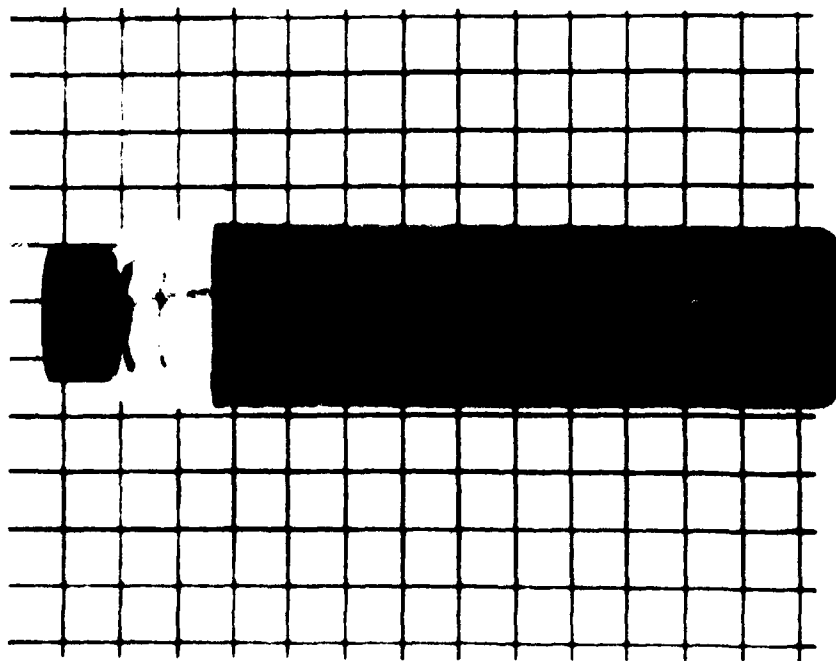
APPENDIX C

FACT SHEETS FOR FIRE-RESISTANT
DIESEL FUEL

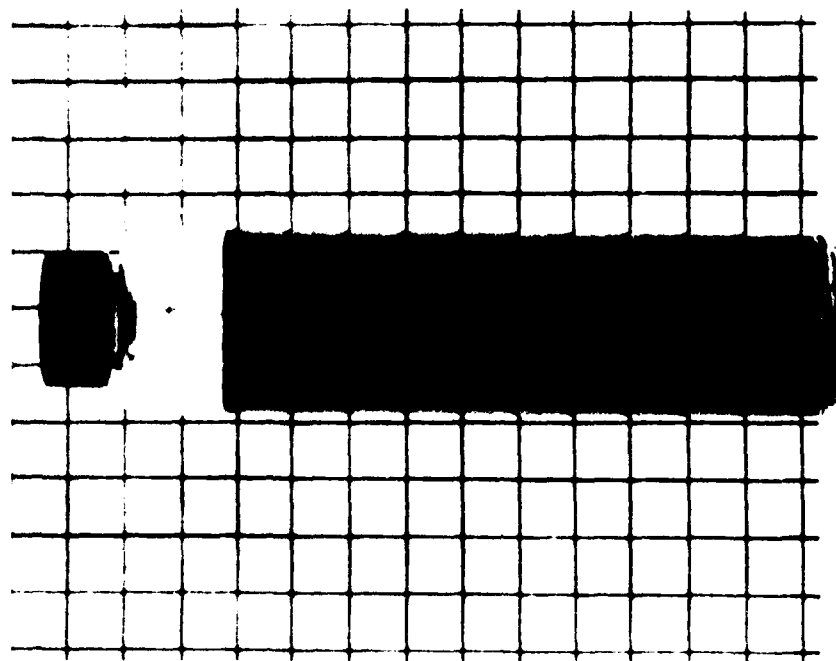
FRF
FACT SHEETS

- Flammability Characteristics of FRF
 - Smaller mist fireball resulting from ballistic penetration.
 - Self-extinguishment of ground fire, thus providing protection for personnel, vehicle and storage facilities.
- Appearance of FRF
 - Clear-to-milky fuel blend
- Composition of FRF
 - 78 vol% Diesel Fuel
 - 6 vol% Emulsifying Agent (EA)
 - 6 vol% Aromatic Concentrate (AC)
 - 10 vol% Water
- Earlier FRF Candidates:
 - FRF-A
 - 84 vol% Diesel Fuel
 - 6 vol% EA
 - 10 vol% Water
 - FRF-B
 - 92 vol% Diesel Fuel
 - 3 vol% EA
 - 5 vol% Water
 - 0.2 wt% Antimist Agent
- Fire Vulnerability Tests
 - Flame Spread Test
 - Impact Dispersion Test
 - AFLRL 20-mm HEIT Ballistic Test
 - Full-Scale Ballistic Test M-113A, M48
- ALFLR 20-mm HEIT Ballistic Test revealed that engine recycled FRF-B offers no advantage over FRF-A.
 - FRF-B investigation terminated.

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Base Fuel
 Referee-Grade Diesel Fuel
 MIL-F-40162A(MR), Grade II



10% Water in Surfactant-
 Stabilized Referee-Grade
 Diesel Fuel

COMPARISON OF FIRE-RESISTANT FUEL WITH NEAT BASE FUEL
 FIGURE C-1.



Maximum Fireball; Neat Diesel Fuel



Maximum Fireball; 10% Water in
Surfactant-Stabilized Diesel Fuel



Post-Impact Pool Fire; Neat Diesel Fuel

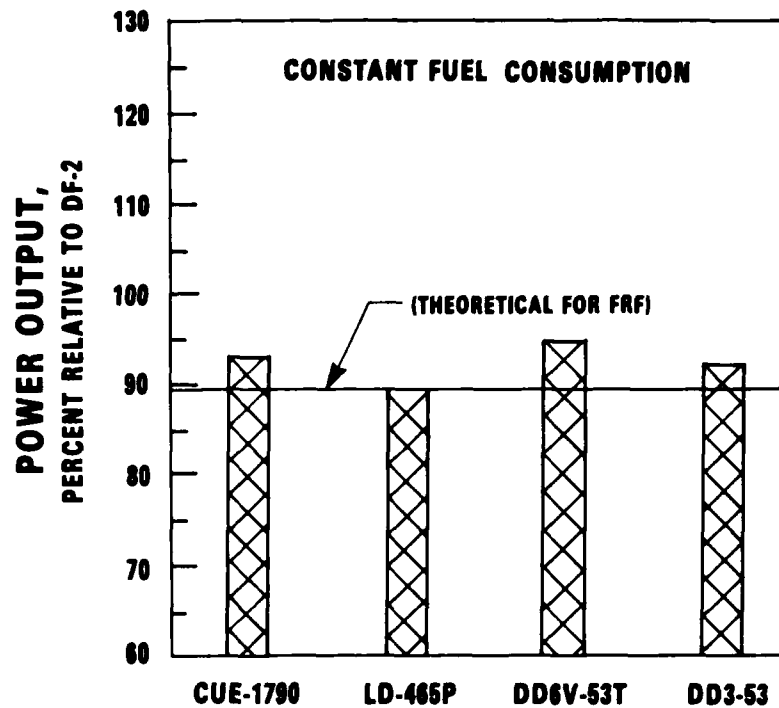


Post-Impact Pool; 10% Water in
Surfactant-Stabilized Diesel Fuel

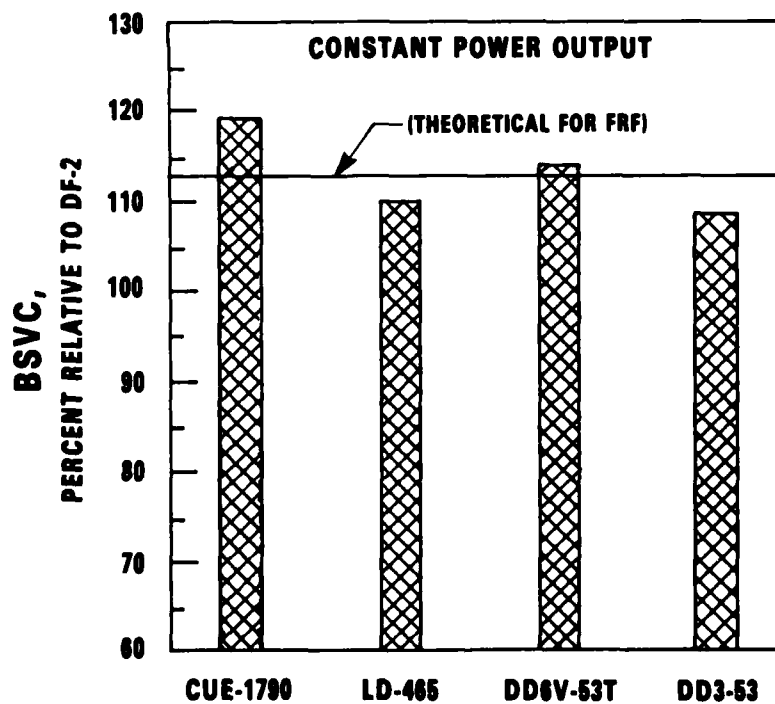
BALLISTIC RESPONSE OF NEAT AND WATER-CONTAINING DIESEL
FUELS AT TYPICAL MAXIMUM OPERATIONAL TEMPERATURE OF
77°C (170°F) [BASE FUEL FLASH POINT OF 63°C (145°F)]

FIGURE C-2.

- Engine Performance/Endurance Tests of FRF
 - Three Single Cylinder Research Engines
 - 43 CID Single-Cylinder CLR Engine
 - CUE (AVDS) 1790 Single-Cylinder Engine Assembly
 - Caterpillar Single-Cylinder Test Engine
 - Multicylinder Unmodified Engines
 - DD3-53
 - DD6V-53T
 - AVDS-1790-2C (Endurance Test)
 - LDT-465-1C
 - Turbine Combustor Performance
 - AFLRL Tests
 - Purdue Tests
- Diesel Engines Will Start, Run, and Idle Satisfactorily on FRF
 - Volumetric net heat of combustion is 11% lower with FRF
 - Rated power is decreased with FRF at original maximum rack setting
 - Rated power recoverable by adjustment of maximum rack setting (resulting in increased total fuel consumption)
- Single-cylinder AVDS 1790-2C FRF Endurance Tests
 - Engine Tests:
 - 250-Hour test using referee grade base fuel
 - 250-Hour test using FRF prepared with deionized water
 - 250-Hour test using FRF prepared with tap water
 - Test Conditions:
 - Constant speed
 - Constant equal loads
 - Performance Effects:
 - No difficulties with starting, idling, or running
 - No change in engine friction during test
 - No performance degradation during test
 - Fuel-Related Mechanical Effects:
 - Normal wear
 - Reduced deposits
 - No corrosion



DIFFERENT ENGINES



DIFFERENT ENGINES

FIGURE C-3. BSVC AND POWER OUTPUT

ALLISON T-63 TURBINE COMBUSTOR FACILITY

		<div> <div>37°C INLET AIR</div> <div>1.4 atm INLET PRESSURE</div> <div>0.18 kg/sec AIR FLOW RATE</div> </div>				NO _x EMISSIONS		100% POWER		100% POWER	
JET A	0.035	F/A FOR		COMBUSTION		G/KG FUEL		FLAME RADIATION		EXHAUST SMOKE	
		10% POWER	100% POWER	40% POWER	100% POWER	10% POWER	100% POWER	(RELATIVE TO DF-2)	(RELATIVE TO DF-2)	(RELATIVE TO DF-2)	(RELATIVE TO DF-2)
JET A	0.035	0.006	0.003	97.3	> 98.1	1.8	6.2	—	—	—	—
DF-2	0.035	0.006	0.002	96.8	> 98.1	—	—	100%	100%	100%	100%
FRF	0.05-0.06	0.007	0.003	93.3	> 98.1	6.5	10.9	65%	65%	50%	50%

FIGURE C-4. ALLISON T-63 TURBINE COMBUSTOR FACILITY

- Energy Conversion Effects (Different for different engines)
 - Engine thermal efficiency: 0-2% More (Benefit)
 - Total energy consumption: 0-4.5% Less (Benefit)
 - Range at maximum power: 7-11% Less (Penalty)
- FRF Fuel/Surfactant/Water Variables
 - 33 different base fuels:
 - DF-2, DF-1, DF-A, NATO F-54
 - Varying types fuel properties:
 - Distillation Range
 - Density
 - Flash Point
 - Total Aromatic Ring Carbon Content (TARC)
 - Surfactant
 - Amide/amine/soap emulsifier
 - Aromatic concentrate solvent
 - Three different Levels of Total Acid Number (TAN)
 - Water Composition:
 - Typical range from 0-500 ppm total dissolved solids (TDS)
 - TDS should be less than 50 ppm and low TAN surfactant should be used
- FRF Blending Requirements
 - Emulsifying Agent (EA) dissolved in equal volume of aromatic concentrate (AC) by simple mixing
 - Surfactant mixture (EA plus AC) dissolved in base fuel by simple mixing
 - Water added to surfactant-containing base fuel by simple mixing.
 - FRF can be made at various temperatures between 0° to 50°C. Some compositions form macroemulsions at 0°C. However, these usually become microemulsions when allowed to warm up to normal ambient temperature (25°C)
- Effects of FRF Formulation on Fuel Properties
 - Acceptable accelerated stability
 - Decrease of about ten cetane numbers

- Viscosity increase of:
 - 1.50 to 50-fold at 10°C
 - 1.5 to 2.6-fold at 20°C
 - 1.4 to 1.5-fold at 30°C
 - 1.4 to 1.5-fold at 40°C
 - 1.5-fold at 50°C
- FRF Storage Stability
 - Constant Temperature (Two base fuels)

4°C	6 months
24°C	6 months
40°C	one month
 - Temperature Cycling [Three base fuels, two water TDS (50 ppm and 300 ppm)]
 - Six cycles:

50°C	22 hours
27°C (Room Temp.)	4 hours
2°C	22 hours
27°C (Room Temp.)	4 hours
 - Some phase separation at 2°C, but FRF became translucent microemulsion at room temperature. No ill effects due to temperature cycling.
- FRF Low-Temperature Filterability
 - Simulated DD6V-53T fuel system was developed for low-temperature pumpability/filterability tests:
 - All FRF's experienced cavitation caused by filter plugging on suction side of the fuel pump at temperatures below 0°C.
 - No suitable additive has been found yet to alleviate this problem. Various anti-freeze, anti-icing, flow-improver, pour-point depressants or wax-crystal modifiers were tested.
- Effects of Diesel Fuel Additives on FRF
 - No adverse affects on phase stability due to:
 - Cetane number improvers
 - Antioxidants
 - FS Icing inhibitors, (e.g., EGME)

- Corrosion inhibitors
 - Dilution with 20% more water (i.e., 2 vol% more)
 - Dilution with other base fuel(s)
 - Dirt contamination-up to 1000 ppm standard dust
 - Rust contamination (Reagent-grade Fe_2O_3)
- FRF Materials Compatability
 - Noncorrosive to
 - Iron
 - Stainless steel
 - Aluminum
 - Corrosive to:
 - Copper
 - Brass
 - Bronze
 - Aryltriazole corrosion inhibitor: concentration of 500-1000 ppm helps reduce copper and brass alloy corrosion
- FRF Quality Assurance Methods
 - Visual-translucency (pass/fail type)
 - Spectral absorbance in 400-600 nm wavelength region (pass/fail type)
 - Dielectric constant (pass/fail type could show absence of a component)
 - Analytical/quantitative
 - Water content by Karl Fischer
 - Heat of adsorption
- Excess Water Tolerance
 - Up to 11 or 12 vol% water content, depending on TDS, TAN and TARC
- Excess Base Fuel Tolerance
 - Dilution with 10 to 90 vol% of same or difference DF-2 not harmful to FRF stability
 - Dilution with more than 20 vol% excess base fuel may defeat self-extinguishing capability of FRF

APPENDIX D

LIST OF EMULSIFYING
AGENTS REFERENCED IN
THIS REPORT

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EMULSIFYING AGENTS REFERENCED
IN THIS REPORT

<u>EA No.</u>	<u>Code No.</u>	<u>Manufacturer</u>	<u>Mfg's Batch No.</u>	<u>Mfg's I.D.</u>	<u>TAN, mg KOH/g</u>
37	7816	Scher	--	ODA+2.5%OA*	18.5, 20.0
78	9438	Clintwood	6782	LT-19-21-1	15.5
79	9443	Scher	M0203	ODA-25	19.0
89	1000-1	Clintwood	6905	LT-19-21-2	19.0
90	1000-2	Clintwood	6906	LT-19-21-2	19.0
96	10360	Clintwood	6905	LT-19-21-2	19.0
97	--	Clintwood	--	50 vol% EA 78+	17.1
				50 vol% EA 89	
98	10452	Clintwood	7078	LT-19-21-2	15.5
99	10484	Clintwood	7081	LT-19-21-1	15.5

*OA refers to added oleic acid

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LIST OF ABBREVIATIONS, ACRONYMS, AND DEFINITIONS

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Organization Acronyms

AFLRL	-	U.S. Army Fuels and Lubricants Research Laboratory
ASTM	-	American Society for Testing Materials
CA	-	Chemical Abstracts, Published by the American Chemical Society
MERADCOM	-	U.S. Army Mobility Equipment Research and Development Command
NACE	-	National Association of Corrosion Engineers
NTIC	-	National Technical Information Center
TACOM	-	U.S. Army Tank-Automotive Command

Technical Acronyms

AC	-	Aromatic Concentrate
BSVC	-	Brake Specific Volumetric Fuel Consumption, e.g., Liters/J
BTX	-	Benzene, Toluene, Xylene Bottoms (C ₉ + Aromatics)
CID	-	Cubic Inches Displacement
CN	-	Cetane Number
DEGME	-	Diethylene Glycol Monomethyl Ether
DTA	-	Differential Thermal Analysis
EA	-	Emulsifying Agent (Surfactant)
EGDME	-	Ethylene Glycol Dimethyl Ether
EGME	-	Ethylene Glycol Monomethyl Ether
EP	-	End Point Distillation
FFD	-	Frozen Fuel Detector
FIA	-	Fluorescence Indicator Analysis
FID	-	Free Induction Decay (in NMR)
FRF	-	Fire-Resistant Fuel
GC	-	Gas Chromatography
HEIT	-	High-Explosive Incendiary-Tracer
HPLC	-	High-Pressure Liquid Chromatography
IBP	-	Initial Boiling Point of Distillation
IR	-	Infrared Spectroscopy
KF	-	Karl Fischer Analysis for Water

LCR - Inductance, Capacitance, and Resistance
 LOA - Letter of Agreement
 LSS - Liquid Solid Separator
 NMR - Nuclear Magnetic Resonance
 O/W - Oil-in-Water
 PCS - Photon Correlation Spectroscopy (Quasi-Elastic Light Scattering)
 PMCC - Pensky Martens Closed Cup Flash Point Test
 TAN - Total Acid No., mg KOH/g
 TARC - Total Aromatic Ring Carbon
 TBN - Total Base No., mg KOH/g
 TDS - Total Dissolved Solids, ppm
 TEG - Triethylene Glycol
 TGA - Thermogravimetric Analysis
 USP - U.S. Pharmaceutical Purity
 UV - Ultraviolet Spectroscopy
 W/O - Water-in-Oil
 XRF - X-ray Fluorescence Spectroscopy

Engine Abbreviations:

AVDS-1790-2C - Teledyne-Continental Twelve-cylinder M60 Battle Tank Engine
 CUE-1790 - Single-cylinder AVDS-1790-2C Laboratory Engine
 DD6V-53T - Detroit Diesel V-6 Two-Stroke Cycle Diesel Engine (Turbocharged)
 DD3V-53 - Detroit Diesel 3-Cylinder Two-Stroke Cycle Diesel Engine
 LDT-465 - U.S.-Army-Designed Multifuel Diesel Engine (Turbocharged)

Vehicle Abbreviations:

M48 - M48 Battle Tank
 M60 - M60 Battle Tank
 M113 - M113 Armored Personnel Carrier

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ALEXANDRIA VA 22314

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ALEXANDRIA VA 22314

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CAMERON STA
ALEXANDRIA VA 22314

COMMANDER
DEFENSE GENERAL SUPPLY CTR
ATTN: DGSC-SSA 1
RICHMOND VA 23297

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OFC OF SEC OF DEF
ATTN USD (R&E)/RTI (DR YOUNG) 1
WASHINGTON, DC 20301

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DALO-AV 1
DALO-SMZ-E 1
DAMA-CSS-P (DR BRYANT) 1
DAMA-ARZ (DR CHURCH) 1
WASHINGTON DC 20310

CDR
U.S. ARMY MOBILITY EQUIPMENT
R&D COMMAND
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DRDME-WC 2
FORT BELVOIR VA 22060

CDR
US ARMY MATERIEL DEVEL&READINESS
COMMAND
ATTN: DRCLD (MR BENDER) 1
DRCDMR (MR GREINER) 1
DRCDMD-ST (DR HALEY) 1
DRCQA-E 1
DRCDE-SG 1
DRCIS-C (LTC CROW) 1
DRCSM-P 1
5001 EISENHOWER AVE
ALEXANDRIA VA 22333

CDR
US ARMY TANK-AUTOMOTIVE CMD
ATTN DRSTA-NW (TWVMO) 1
DRSTA-RG (MR HAMPARIAN) 1
DRSTA-NS (DR PETRICK) 1
DRSTA-G 1
DRSTA-M 1
DRSTA-GBP (MR MCCARTNEY) 1
WARREN MI 48090

DIRECTOR
US ARMY MATERIEL SYSTEMS
ANALYSIS AGENCY
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DRXSY-S 1
DRXSY-L 1
DRXSY-F 1
ABERDEEN PROVING GROUND MD 21005

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U.S. ARMY R&T LAB (AVRADCOM)
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DAVDL-ATL-ASV (MR CARPER) 1
FORT EUSTIS VA 23604

HQ, 172D INFANTRY BRIGADE (ALASKA)
ATTN AFZT-DI-L 1
AFZT-DI-M 1

DIRECTORATE OF INDUSTRIAL
OPERATIONS
FT RICHARDSON AK 99505

CDR
 US ARMY GENERAL MATERIAL &
 PETROLEUM ACTIVITY
 ATTN STSGP-F (MR SPRIGGS) 1
 STSGP-PE (MR MCKNIGHT),
 BLDG 85-3 1
 STSGP (COL CLIFTON) 1
 NEW CUMBERLAND ARMY DEPOT
 NEW CUMBERLAND FA 17070

CDR
 US ARMY MATERIEL ARMAMENT
 READINESS CMD
 ATTN DRSAR-LEM 1
 ROCK ISLAND ARSENAL IL 61299

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 (EUROPE)
 ATTN DRXSN-UK-RA 1
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 DRDAV-D (MR CRAWFORD) 1
 DRDAV-N (MR BORGMAN) 1
 DRDAV-E 1
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 ST LOUIS MO 63120

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 AFLG-POP 1
 FORT MCPHERSON GA 30330

CDR
 US ARMY ABERDEEN PROVING GROUND
 ATTN: STEAP-MT 1
 STEAP-MT-U 1
 ABERDEEN PROVING GROUND MD 21005

CDR
 US ARMY YUMA PROVING GROUND
 ATTN STEYP-MT (MR DOEBBLER) 1
 YUMA AZ 85364

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 TERMINAL BALLISTICS BLDG. 393 1
 ABERDEEN PROVING GROUND, MD 21005

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 OFC OF PROJ MGR, ABRAMS TANK SYS
 ATTN DRCPM-GCM-S 1
 WARREN MI 48090

MICHIGAN ARMY MISSILE PLANT
 PROG MGR, FIGHTING VEHICLE SYS
 ATTN DRCPM-FVS-SE 1
 WARREN MI 48090

PROJ MGR, M60 TANK DEVELOPMENT
 USMC-LNO, MAJ. VARELLA 1
 US ARMY TANK-AUTOMOTIVE CMD (TACOM)
 WARREN MI 48090

PROG MGR, M113/M113A1 FAMILY
 OF VEHICLES
 ATTN DRCPM-M113 1
 WARREN MI 48090

PROJ MGR, MOBILE ELECTRIC POWER
 ATTN DRCPM-MEP-TM 1
 7500 BACKLICK ROAD
 SPRINGFIELD VA 22150

OFC OF PROJ MGR, IMPROVED TOW
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 US ARMY TANK-AUTOMOTIVE R&D CMD
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 HQ, US ARMY ARMAMENT R&D CMD
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